1990

Speciation and Redox Chemistry of Selenium and Arsenic in Wetland Soils and Sediments.

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Order Number 9123219

Speciation and redox chemistry of selenium and arsenic in wetland soils and sediments

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The Louisiana State University and Agricultural and Mechanical Col., 1990

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SPECIATION AND REDOX CHEMISTRY OF SELENIUM AND ARSENIC IN WETLAND SOILS AND SEDIMENTS

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Marine Sciences

by

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December 1990

ACKNOWLEDGEMENTS

I wish to express my sincere appreciation to Dr. W.H. Patrick, Jr., Boyd Professor of Marine Sciences, and Director of the Laboratory for Wetland Soils and Sediments, for his guidance throughout the course of my graduate studies at the Louisiana State University. His experience and suggestions were invaluable, and contributed insights that are reflected in this work.

Special appreciation is expressed to Dr. R.D. Delaune, for his assistance and many helpful suggestions throughout this study.

Special thanks are also extended to my committee: Dr. W.H. Patrick, Jr., Dr. J.S. Hanor, Dr. R.D. Delaune, Dr. R.P. Gambrell, Dr. E.N. Lambremont, Dr. I.A. Mendelssohn, and Dr. S.P. Meyers, for their academic expertise and review of the manuscript.

I also would like to thank everyone in the Laboratory for Wetland Soils and Sediments, for their friendship and support during my three-year stay at Louisiana State University. Special thanks go to Mr. J.H. Pardue for reviewing and carefully editing many parts of this manuscript.

Finally, heartful thanks go to my wife, Elly, for her love and understanding, which enabled me to continue during times when the unique nature of selenium and arsenic compounds would have discouraged even the most avid researcher.

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ABSTRACT

Studies dealing with the speciation, species transformations, and solubility of selenium and arsenic as affected by soil or sediment redox potential and pH were initiated because of a lack on information and the need for a better understanding of selenium and arsenic chemistry in wetland soils and sediments. Analytical techniques were developed that permitted the determination of selenium and arsenic species commonly encountered in soils and sediments. The speciation and redox chemistry of selenium and arsenic was studied in selected soils and sediments.

Under reduced conditions (-200 mV), selenium solubility in sediments from Kesterson Reservoir (CA) and Hyco Reservoir (NC) was low and [elemental selenium + selenides] comprised 80 - 100 % of the total soluble selenium. Experimental data and equilibrium thermodynamic calculations suggest that insoluble metal selenides, particularly FeSe, controlled selenium solubility under reduced conditions. Upon oxidation form -200 to 500 mV selenium solubility increased approximately 20 times in both the Kesterson and Hyco Reservoir sediments. Under moderately reduced conditions (0 - 200 mV), selenite was the dominant (45 to 100 %) soluble selenium species. At redox levels above 200 mV, selenite was further oxidized to selenate and selenium solubility reached a maximum. An alkaline pH resulted in greater dissolved selenium concentrations. The experimental data also illustrated the importance of biomethylation in selenium chemistry. Under oxidized conditions, dimethyl selenide constituted 15 to 36 % of the total soluble selenium.

Redox potential and pH were also shown to exhibit a major impact on arsenic speciation, and solubility in Hyco Reservoir (NC) sediments and in an arsenic contaminated soil from Kolin (La). In contrast to

selenium, arsenic solubility increased with decreasing redox. In both studies, arsenate was the major (> 80 %) arsenic species present under oxidized conditions. Upon reduction, arsenite became the major dissolved arsenic species, and arsenic solubility increased. Upon reduction from 500 to -200 mV, total arsenic in solution increased 25 and 13 times in the Hyco Reservoir and Kolin soil, respectively. The importance of adsorption-desorption and precipitation-dissolution reactions in controlling arsenic chemistry was illustrated in the Kolin soil.

INTRODUCTION

1. Sources of arsenic and selenium

Arsenic (As) and selenium (Se) are derived from the weathering of rocks and soils or are introduced into the atmosphere by volcanic activity. Limestones and sandstones tend to have low concentrations of both As and Se (typically < 0.1 mg kg^{-1}), whereas shales tend to have higher concentrations (Lakin and Davidson, 1973; Onishi and Sandell, 1955). Sulfide ores often contain As and/or Se. While As has been asssociated with a variety of heavy metal sulfides (Boyle and Jonasson, 1973), galena and pyrite are the principal hosts for Se (Nazarenko and Ermakov, 1972). The weathering of these sulfides can give rise to locally high concentrations of As or Se. The average concentration of As and Se in soils is estimated to be 2 (Onishi and Sandell, 1955) and 0.05 mg kg^{-1} (Swaine, 1955), respectively. The Se-enriched Pierre Shale, formed during the Cretaceous period, is the parent material for the seleniferous soils (1-150 mg Se kg^{-1}) of the Great Plains of the USA (Tanji et al., 1986). During volcanic activity, As and Se escape into the atmosphere as high-temperature volatile gases where they are washed out by rain into surface waters (Peterson, 1980; Reuter, 1975). Most natural waters tend to have low concentrations of As (< 0.05 mg L^{-1}) and Se (< 0.01 mg L^{-1}). At the present time, the contribution of vulcanism to concentrations of As and Se into the environment is small in comparison to the contribution due to weathering. However, volcanic activity has added much to the sedimentary As and Se concentrations over geological times (Reuter, 1975).

Increasingly, As and Se are being introduced into the environment by human activities. Elevated As and Se concentrations are associated with the burning of fossil fuels (Ferguson and Gavis, 1972; Piver, 1983), coal and petroleum by-products including coal fly-ash (Campbell et al., 1978; White et al., 1984), refining of metal ores (Lakin and Davidson, 1973), mine tailings (Thompson and Heggen, 1982), and agricultural drainage (Deverel et al., 1984). Arsenic is also a component of pesticides, herbicides and fungicides (Moore and Ramamoorthy, 1984). Selenium is frequently added in trace amounts to fertilizers (Korkman, 1985). Coal often contains up to 50 mg Se kg^{-1} (Adriano, 1986) and up to 100 mg As kg^{-1} (Piver, 1983). Combustion of coal is believed to be the major anthropogenic process leading to increased As and Se concentrations (Andren et al., 1975). In addition, As and Se discharged in fly ash by coal-fired power plants can cause severe effects on fish populations and wildlife in the reservoirs receiving effluents (Lemly, 1985; Woock and Summers, 1984). For example, increased As and Se concentrations in the Hyco Reservoir (NC), the cooling water source for a coal-fired electric plant, has led to the elimination of several fish species.

World-wide attention was focused on Se in the environment in the mid-1980s, when subsurface agricultural drainage waters were used for the creation and management of wetlands in Kesterson Reservoir National Wildlife Refuge in California. Studies at the Kesterson Reservoir have shown that Se bioaccumulated in plants and animals at levels that adversely affected wildlife (Davis et al., 1988; Ohlendorf, 1989). These findings led to extensive research on the behavior of Se in the environment.

2. Importance of arsenic and selenium speciation

Arsenic is toxic to most living organisms. It may inhibit metabolic reactions by combining with the sulfhydryl groups of key enzymes (White et al., 1973), or uncouple oxidative phosphorylation by substituting for phosphate (Stryer, 1981). Trivalent and pentavalent As differ in their toxicity. Unlike As(III), the As(V) species do not react directly with the active sites of enzymes (Pauwels et al., 1965). Organic arsenicals exert their toxicity after being reduced in vivo to As(III) (Peters, 1955). Selenium is of considerable biological interest because it is required by animals, but it can also be very toxic. The major mechanism of Se toxicity is its substitution for S in many proteins resulting in a destabilization of the Se-substituted compounds (Shrift, 1973). Selenium has also been reported to inhibit terminal cytochrome oxidase, and to readily denaturate sulfhydryl enzymes (Martin, 1973). The toxicity of Se compounds varies greatly, but soluble inorganic Se forms are considered to be the most toxic (Davis et al, 1988). The formation of organic Se compounds by animals is thought to be a detoxification mechanism (Doran, 1982). The toxicity of methylated Se compounds is about 1/500 to 1/1000 of the toxicity of the inorganic species (Vokal-Borek, 1979).

Recognition that different As and Se compounds vary in their toxicities has directed attention towards the specific compounds or chemical forms of the elements. Over the years it has become evident that studies concerning speciation and species transformations are not only important in assessing the toxicity, but essential to understanding the behavior of trace elements in the environment. Indeed for any calculation involving chemical equilibria, adsorption, transport, or plant uptake, it is necessary to know the chemical form in which an

element is present. Identification and quantification of chemical forms of trace elements, such as As and Se, is often difficult because of the small amounts of the elements present and the complex composition of most natural waters.

In natural waters, soils, and sediments, the As species of interest are the arsenate oxyanions [H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-}; As(V)], the arsenite oxyanions [H_3AsO_3, $H_2AsO_3^-$, $HAsO_3^{2-}$, and AsO_3^{3-}; As(III)], monomethylarsonic acid [$(CH_3AsO(OH)_2$, As(III)], and dimethylarsinic acid [$(CH_3)_2AsO(OH)$, As(I)]. Inorganic Se in natural waters, soils, and sediments can exist as selenate [H_2SeO_4, $HSeO_4^-$, and SeO_4^{2-}; Se(VI)], selenite [H_2SeO_3, $HSeO_3^-$, and SeO_3^{2-}; Se(IV)], as colloidal elemental Se [Se(0)], and as selenide [H_2Se, HSe^-, and Se^{2-};Se(-II)]. Organic forms of Se are analogous to those of S and include seleno amino acids [e.g. selenocysteine, and selenomethionine], methyl selenides [e.g. $(CH_3)_2Se$], and methyl selenones [e.g. $((CH_3)_2SeOO$].

The biogeochemistry of As (Boyle and Jonasson, 1973; Braman, 1975; Ferguson and Gavis, 1972) and Se (Adriano, 1986; Allaway, 1968; Rosenfeld and Beath, 1964) has been reviewed in detail by many researchers. All authors agree that As and Se biogeochemistry is complex, and not completely understood. Arsenic and Se chemistry is governed by many factors. The solubility of their salts, the complexing ability of solid and soluble ligands, biological reactions, and pH and redox conditions are all reported to control As and Se concentrations and speciation. Equilibrium solubility and speciation information on As and Se have been summarized and graphically displayed in redox-pH and related diagrams. Ferguson and Gavis (1972) presented a redox-pH diagram that clearly illustrates the stability of the different As species.

Sadiq et al. (1983) used an equilibrium thermodynamic approach and developed solubility isotherms for several As minerals. Recently, Elrashidi et al. (1987) developed solubility relationships for 83 Se minerals and soluble Se species in soils. These diagrams have been used by a number of investigators to predict and explain various aspects of As and Se biogeochemistry.

As a result of biological conversions, however, the thermodynamically predicted species are often transformed to kinetically stabilized metabolites. Furthermore, details of constructed pe-pH diagrams depend critically on the assumptions made about ion activities and complexing agents (Drever, 1988). Although theoretically derived predictions are useful in obtaining a general understanding of As and Se chemistry, an exact interpretation of the biogeochemical factors influencing the environmental behavior of As and Se requires detailed experimental studies.

Several investigators suggest that As and Se chemistry is mainly governed by adsorption-desorption reactions rather than by precipitation-dissolution reactions (Balistrieri and Chao, 1987; Livesey and Huang, 1981). The adsorption behavior of the different As (Elkhabtib et al., 1984; Holm et al., 1980) and Se (Neal et al., 1987a, b, ; Neal and Sposito, 1989) species on mineral surfaces and soils has been extensively studied. Convincing evidence for a species specific adsorption behavior has been presented. It is important to note that in all of these studies one particular As or Se species was used. Moreover, possible transformations among species during the time period of the experiments was neglected.

Although redox potential and pH are thought to be the most important parameters governing As and Se chemistry (Cary and Allaway, 1969; Elrashidi et al., 1987; Ferguson and Gavis, 1972; Geering et al., 1968; Sadiq et al., 1983), few studies have experimentally investigated, probably due to a lack of suitable analytical techniques, the effect of redox potential and pH on As and Se speciation and chemistry. Soils and sediments can experience redox conditions ranging from - 200 to + 600 mV. In oxidized (aerobic) soils or sediments, redox potential (Eh) is reported to range from about + 400 to + 600 mV. When soils or sediments are inundated with water, continued oxygen demand of microorganisms and plant roots rapidily deplete the oxygen content and reduced conditions usually result. Upon flooding, various chemical and biological transformations take place resulting in a decrease in Eh. In most reduced (anaerobic) sediments and submerged soils, the Eh ranges from around - 300 to + 100 mV. Moderately reduced soils or sediments are characterized by an Eh between +100 and +400 mV (Gambrell and Patrick, 1978). The pH of both acid and alkaline oxidized soils and sediments tends to converge toward pH 7 when these soils or sediments become reduced (Patrick and Mikkelsen, 1971). After a flooded soil or inundated sediment is allowed to drain, O_2 reenters the system and oxidation processes occur. There is usually a thin layer of oxidized soil (sediment), sometimes only a few millimeters thick, at the surface of flooded soils or at the sediment - water interface (Patrick and Delaune, 1972). This thin oxidized layer is reported to be very important in the chemical transformations and nutrient cycling that occur in wetlands (Mitsch and Gosselink, 1986).

Changes in the physicochemical properties (e.g. pH, and redox potential) of soil and sediment-water systems due to flooding or drainage often influence the chemical behavior and the bioavailability of nutrients (Patrick and Khalid, 1974; Patrick and Reddy, 1976) and toxic heavy metals (Gambrell et al., 1976a, b). Presently, little quantitative data are available on the distribution, and stability of As, and especially Se species in soils and sediments under different redox and pH conditions. Information on the kinetics of the reactions involved is completely lacking.

3. Research objectives

Both the lack of experimental data and the importance of a better understanding of the chemistry of As and Se in wetland soils and sediments warrant studies of the effect of redox potential and pH on As and Se speciation and solubility. In this dissertation an attempt was made to experimentally measure and evaluate the influence of soil or sediment redox potential and pH on the transformations and solubility of As, and Se species as a step forward toward quantitative predictions of their environmental chemistry. The principal objectives of the research were to:

1) Develop analytical methods that permit the determination of As and Se species commonly encountered in natural waters, soils, and sediments.
2) Study the speciation and transformations of As and Se, using the developed speciation techniques, in soils and sediments as affected by redox potential and pH.

3) Learn more about the biogeochemical processes controlling As and Se speciation, and solubility in soils and sediments.

Much effort was put in the development and testing of analytical methods suitable for determining soluble As and Se species. The analytical techniques which have been developed and used for Se and As speciation are presented in chapters 1 and 2, respectively. The second and third objectives were accomplished by studying, under laboratory conditions, the redox chemistry of As and Se in selected sediments and soils. Selenium speciation and transformations among species as affected by redox potential and pH were studied in Kesterson Reservoir (CA) and Hyco Reservoir (NC) sediment suspensions. Arsenic speciation and redox chemistry was studied in Hyco Reservoir (NC) sediment suspensions and in an arsenic contaminated soil from Kolin (La). The speciation and redox chemistry of Se in Kesterson Reservoir sediments is reported in chapter 3. Based on the experimental data obtained in chapter 3, selected thermodynamic data were used to predict Se behavior in anoxic sediments and soils. Results from equilibrium thermodynamic calculations and constructed redox-pH stability diagrams for the system Fe-Se-S-H_2O are summarized in chapter 4. Chapter 5 deals with the speciation and solubility of As and Se in Hyco Reservoir sediments as affected by sediment redox potential and pH. The speciation and redox chemistry of As in a contaminated soil from Kolin is presented in chapter 6.

The six chapters of this dissertation were written in manuscript form and submitted to refereed journals. Chapter 1 is accepted for publication in Spectroscopy Letters (Vol. 24, No 2). Chapter 2 is accepted for publication in the Journal of Environmental Quality and is

scheduled to appear in the January, 1991 issue. Chapter 3 was published in Environmental Science and Technology (P.H. Masscheleyn, R.D. Delaune, and W.H. Patrick, Jr. 1990. Transformations of selenium as affected by sediment oxidation-reduction potential and pH. Environ. Sci. Technol., 24, 91-96). Chapter 4 is accepted for publication in Toxic and Hazardous Substance Control, which appears in special editions of the Journal of Environmental Science and Health. The other manuscripts are currently being reviewed.

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CHAPTER I

SELENIUM SPECIATION IN AQUEOUS SOLUTIONS USING A HYDRIDE GENERATION ATOMIC ABSORPTION SPECTROPHOTOMETRY TECHNIQUE.

ABSTRACT

A sensitive analytical technique for the determination of soluble selenium species [Se(IV), Se(VI), Se(0,-II), dimethyl selenide (DMSe), and oxidized methylated organo-Se compounds], using hydride generation atomic absorption spectrophotometry is described. Dimethyl selenide is purged out of a solution and trapped on a U-tube immersed in liquid N_2. After controlled heating of the sample trap, DMSe is quantified in a quartz flame-in-tube atomizer aligned in the optical path of an atomic absorption spectrophotometer. Selenite [Se(IV)] and oxidized methylated Se-compounds are reduced by $NaBH_4$ in 4 M HCl to H_2Se and DMSe, repectively. Entrained by He carrier gas they are trapped in a liquid N_2 cooled U-tube. Their separation is accomplished by controlled heating of the sample trap. Hydrogen selenide and DMSe carried out of the trap into the atomization cell are detected as two distinct and sharp absorption signals. Oxidative and/or reductive chemical digestions are used to quantitatively convert total soluble Se or Se(VI) to Se(IV), while the original Se(IV) stays unchanged. The digestions are analyzed for Se(IV). Selenate [Se(VI)] is calculated from the difference between the Se(IV) and [Se(VI)+Se(IV)] analysis. The difference between the total Se content and the [Se(VI)+Se(IV)] analysis represents the Se(0,-II) fraction. The technique has been applied for Se speciation in sediment-water extracts.

INTRODUCTION

Over the years it has become evident that speciation of selenium (Se) with respect to oxidation state is important in assessing its bioavailability and toxicity (Cutter and Bruland, 1984; Shamberger, 1983). In the environment, inorganic Se can exist in four different oxidation states: selenate (Se(VI)), selenite (Se(IV)), elemental Se (Se(0)), and selenide (Se(-II)). During microbial assimilation oxidized Se species are reduced to various organically bound Se(-II) compounds (i.e. seleno-amino acids), and it is thought that upon regeneration a considerable quantity of the organic Se compounds are converted to dimethyl selenide (DMSe), a volatile metabolite (Doran and Alexander, 1977; Thompson-Eagle and Frankenberger, 1990). Studies of Se species and transformations among species are essential to the understanding of the behavior of Se in the environment. Such studies require techniques capable of speciating and measuring Se levels in various sample matrices.

Hydride generation atomic absorption spectrometry (AAS) has become a well-established technique (Verlinden et al., 1981) for the determination of Se because of its selectivity and sensitivity. Improved detection limits have been realized by collecting and concentration of the hydrides prior to their introduction into the atomization cell. Cryogenic condensation in a U-tube immersed in liquid N_2 has been shown to be extremely useful for this purpose (Cutter, 1978; Siemer and Koteel, 1977). Acidity of the solution and the valency state of Se are of principal importance in the hydride generation technique. Selenium hydride is formed essentially only from Se(IV). Using radiotracers,

McDaniel et al. (1976) found a 4 M HCl concentration to be optimal for H_2Se formation from tetravalent Se. Under these conditions no Se(VI) was found to be converted to the hydride. This selectivity of hydride generation AAS for Se(IV) has been used in combination with oxidative and reductive chemical digestions to determine Se(IV), the sum of Se(IV) and Se(VI), and total Se concentrations in water samples (Cutter, 1978; Cutter and Bruland, 1984; Fio and Fujii, 1990; Yamada and Hattori, 1990). Reagents used in the selective oxidative and reductive chemical digestions have been critically examined by several authors (Brimmer et al., 1987; Bye, 1983; Fio and Fujii, 1990; Krivian et al., 1985) and several procedures are in use. In speciation studies, Se(VI) concentrations are generally determined based on the difference between the Se(IV) and the [Se(IV) + Se(VI)] analyses. The difference between the total Se and the [Se(IV) + Se(VI)] concentration represents the concentration of [Se(-II) + Se(0)] compounds.

Currently, soluble organic Se compounds are determined by gel chromatography (Yamada and Hattori, 1989) in which organically-bound Se fractions are separated based on their molecular weight. Analytical methods for the determination of volatile methylated Se species, i.e. DMSe, involve gas chromatographic techniques. The methods involve either desorption of trapped volatile compounds by solvent elution or direct gas injection (Doran and Alexander, 1977; Lewis et al., 1966; Thompson-Eagle and Frankenberger, 1990). A combined gas chromatography - mass spectrometry technique was used by Francis et al. (1974) to identify and quantify the amount of DMSe evolved from soils amended with Se. Chau et al. (1975) described a combination of a gas chromatograph with an atomic

absorption spectrophotometer for the analysis of DMSe in gaseous samples.

The purpose of this paper is to describe a relative simple analytical technique for the analysis of inorganic Se species, dissolved DMSe and methylated organoselenium compounds at nanogram levels. The technique involves hydride generation, cryogenic condensation, hydride separation based on their boiling points, and quantitation by atomic absorption spectrophotometry. The combination of the newly developed hydride generation/trapping/separation technique and AAS detection is advantageous in that a single apparatus can be used for determination of both inorganic and organic Se compounds. A detailed description of the experimental setup and analytical procedures used is reported. The method was developed primarily to determine soluble Se species in sediment-water extracts and could easily be used for Se speciation in other natural waters. As an evaluation of the technique, results from Se speciation analyses in aerobic and anaerobic sediment-water extracts are included.

MATERIALS AND METHODS

Apparatus

Figure 1 shows the apparatus used for generating, trapping, and separating the hydrides in the Se speciation studies. The system included a helium purged hydride generation vessel, a glass U-tube immersed in an ice bath, a glass U-tube immersed in liquid N_2, and a Perkin Elmer 360 atomic absorption spectrophotmeter (Perkin Elmer Corp., Norwalk, CT) fitted with a flame-in-tube burner. The hydride generation vessel, a gas washing bottle, could hold up to 75 mL. Reagents were

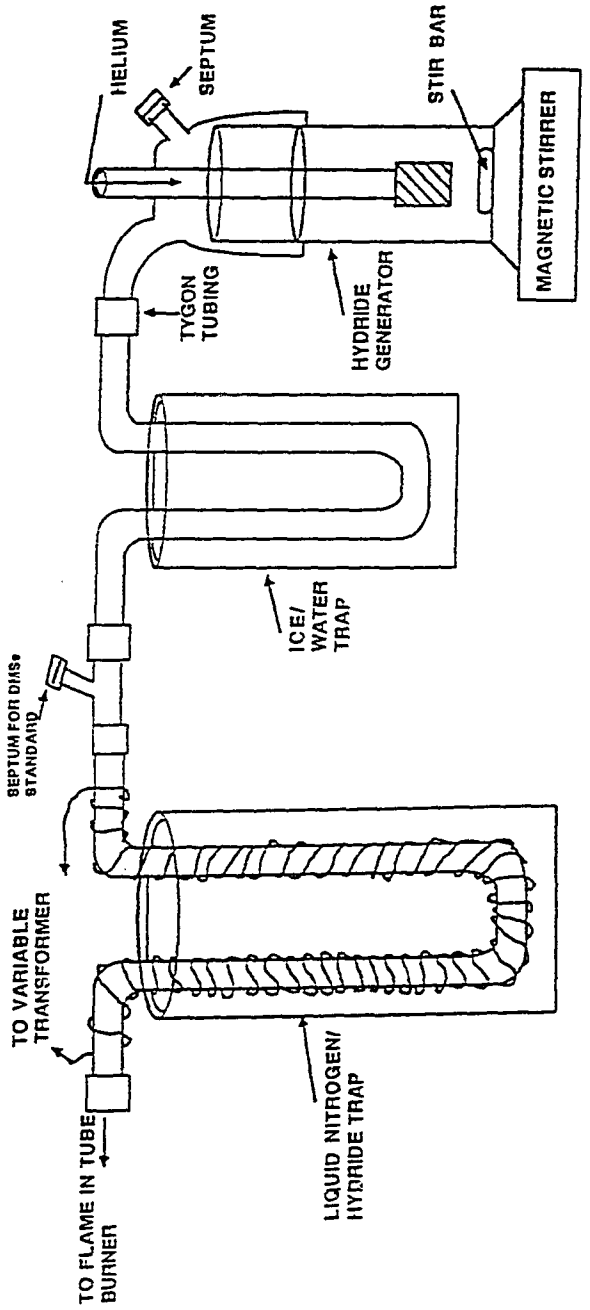

Figure 1: Apparatus used for the generation, trapping, and separation of H_2Se and DMSe.

added through the rubber septum. Helium carrier gas (150 mL min^{-1}) entered the reaction vessel through a fritted glass bubbler. A pyrex U-tube immersed in an ice bath was found to be effective in removing water vapor from the gas stream before it reached the sample trap immersed in liquid N_2. If this drying tube was ommitted the liquid N_2 hydride trap became quickly clogged with ice. The hydride trap consisted of a 40-cm pyrex tube (4 mm i.d.). The tube was wrapped with 1.5 m of 1 mm Nichrome wire (Sargent-Welch, Skokie, IL). The wire, connected to a variable transformator with alligator clips, acted as heating element. An autotransformer setting of 15 V led to a slow warming of the trap, and was used throughout the study. When it was necessary to analyze for DMSe the system was slightly modified. A second septum was installed between the water, and hydride trap (Figure 1). Through this septum gas-phase DMSe standards (see below) were injected. Connections between the reaction vessel, the water and hydride trap were made with Tygon tubing (Nalge Co, Rochester, IL). The outlet of the hydride trap was connected to the auxiliary output of a quartz flame-in-tube burner with teflon tubing.

The stainless steel burner mount and quartz atomization cell (Figure 2) were custom made after a design originally described by Johnston (1978). The quartz cell (length, 12 cm; i.d., 12 mm) burned an air-hydrogen flame (H_2 flow, 280 mL min^{-1}; air flow, 150 mL min^{-1}) and was aligned in the optical beam path of the atomic absorption spectrophotometer. The light source was a Se EDL which was operated at 6 Watts. Absorbance was measured at 196.0 nm. Instrument settings for the atomic absorption spectrophotometer were: slitwidth, 0.7 nm; gain setting, 50 %, and mode, TC1. The output was recorded on a strip chart

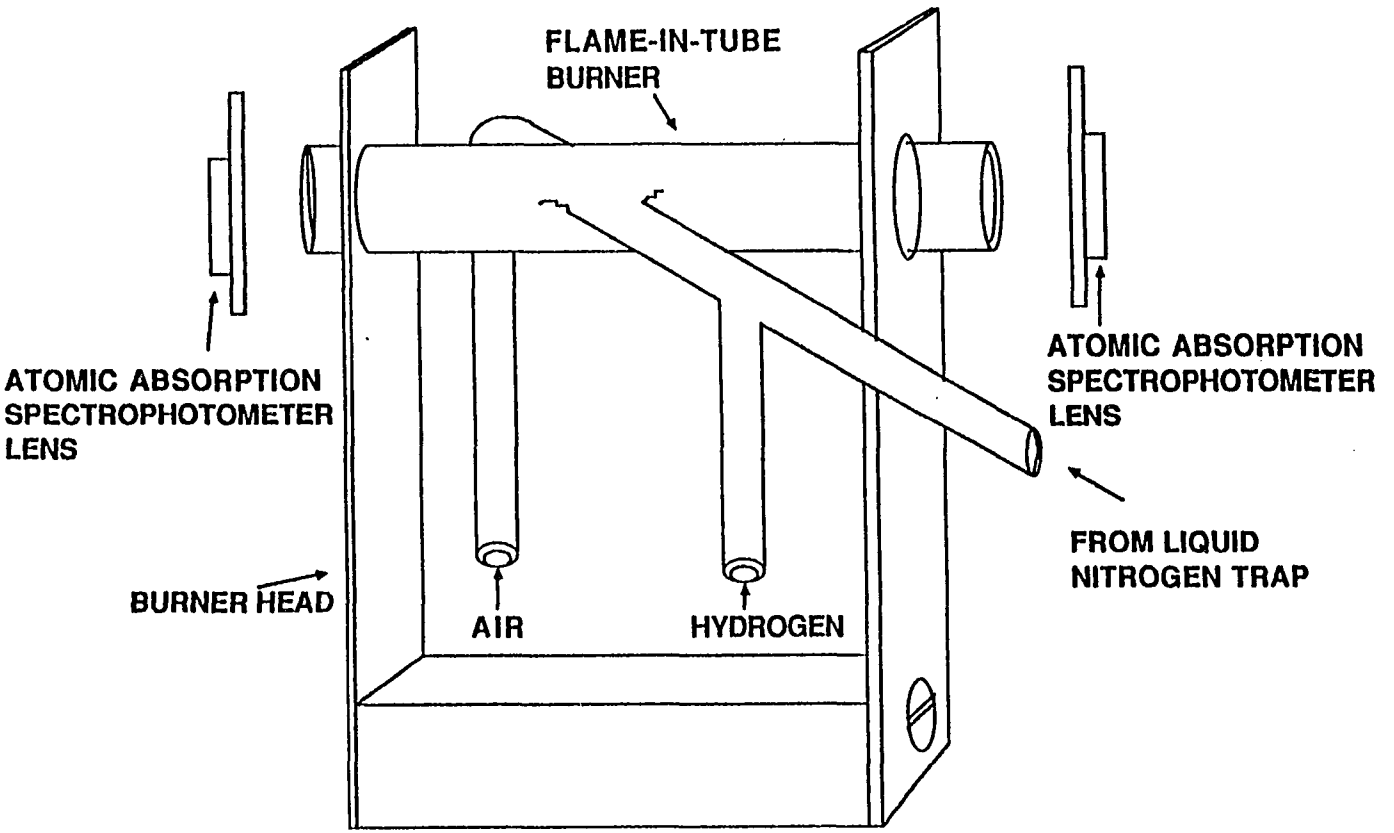

Figure 2: Quartz flame-in-tube atomization cell and stainless steel burner mount.

recorder (Perkin Elmer model 561) operated at 30 mm min^{-1} and peak heights were used to calculate concentrations.

Standards and Reagents

All chemicals used were analytical grade. Selenite and selenate stock solutions (1000 mg Se L^{-1}) were prepared from their sodium salts (Aldrich Chemical Co, Milwaukee, WI). Standard solutions containing 100 ug L^{-1} were diluted daily, or as needed, from intermediate stock solutions of 10 mg Se L^{-1}.

Pure DMSe was obtained from Alfa Chemicals (Danvers, MA), and standard solutions were prepared by dilution with HPLC grade methanol. As DMSe is highly volatile and toxic, the standards were stored in gas-tight vials equipped with Teflon backed rubber septums for withdrawal of liquid aliquots. To avoid the long purging time (up to 20 min) necessary to strip all DMSe form the methanol solutions during standardization of the AAS, a gas-phase DMSe standard was prepared. Ten uL of pure DMSe was added to 5 mL of hexane in a 15 mL gas-tight vacutainer (Becton Dickinson, Rutherford, N.J.) equipped with a rubber septum. A 1 mL volume of DMSe saturated air was withdrawn and injected into pre-evacuated (< 15 mm Hg) 15 mL vacutainers. Working gas-phase DMSe standards were prepared by injecting known volumes of helium gas into the DMSe containing vacutainers. Once the DMSe content of the gas-phase standards was determined using a liquid standard solution, they were used to calibrate the AAS. The use of the diluted gas-phase DMSe standards allowed for a quick (2 min) and reproducible standardization. A 3 % (w/v) solution of $NaBH_4$ was prepared fresh daily by dissolving $NaBH_4$ powder in deionized H_2O. The solution was filtered and stabilized

by adding 4 mL of 2 M NaOH per 100 mL solution. Sulfanilamide, $NaBH_4$, HCl, and $H_2C_2O_4$ used in this study were obtained from Mallinckrodt, Inc. (Paris, KY). Potassium peroxodisulfate was purchased from EM Science (Gibbstown, N.J.). Reagent blanks were processed through identical steps as standards and samples. It was determined that the reagents contributed insignificantly to the Se measured, and that blank corrections were not necessary.

Analytical procedures

Determination of dissolved DMSe

Dimethyl selenide is a volatile liquid and can be easily stripped out of a solution. For the determination of DMSe, 20 mL of distilled deionized H_2O was added to the hydride generation vessel. The system was flushed with helium and the hydride trap was immersed into liquid N_2. After cooling, a sample aliquot was injected through the septum by means of a gas-tight syringe. The DMSe is stripped out of the solution and concentrated on the liquid N_2 trap. Complete removal of DMSe from the aqueous solutions was obtained after 20 minutes. The liquid N_2 was then removed and the trap slowly heated by means of the Nichrome wire wrapped around the trap. The warming of the trap resulted in a volatilization of DMSe. Dimethyl selenide was carried with the helium stream into the atomization cell and detected by AAS. The detection of DMSe by AAS resulted in a single sharp peak with a retention time of approx. 26 seconds. The use of the AAS as detector ensured a Se-compound specific detection. Volatile Se compounds were identified as DMSe based upon retention time and standard addition.

Determination of dissolved Se(IV) and simple dissolved methylated Se compounds

Calibration of the hydride-AAS technique for inorganic Se species was done as follows. Forty five mL of 4 M HCl and the Se(IV) standard were added to the hydride generation vessel. The system was flushed with helium and the hydride trap was immersed into liquid N_2. After cooling, 3 mL of 3 % $NaBH_4$ was slowly injected (3 mL min^{-1}) through the septum into the reaction vessel, while continuously stripping with helium. The H_2Se formed, during the reduction of dissolved Se(IV), is swept out of the solution and trapped on the sample trap immersed in liquid N_2. After 2 min of purging another 1 mL aliquot of $NaBH_4$ was added. This procedure resulted in reproducible H_2Se generation and quantitative trapping of the hydrides on the liquid N_2 trap. The efficiency of the liquid N_2 trap in freezing out the H_2Se was checked by putting a second trap in series. Using the above described apparatus and analytical procedure up to 300 ng of Se could be quantitatively trapped. Six minutes after the initial addition of $NaBH_4$ the liquid N_2 was removed and the trap slowly heated by means of the Nichrome wire wrapped around the trap. The warming of the trap resulted in a volatilization of H_2Se. The hydride was carried with the helium stream into the atomization cell and detected by AAS as a sharp peak with a retention time of approx. 10 seconds.

For the determination of Se(IV) in sample aliquots, the sample was loaded into the hydride generator and the solution acidified with conc. HCl to a pH corresponding to 4 M HCl. Then, the acid-catalyzed $NaBH_4$ reduction procedure described above was followed.

During this analysis simple oxidized methylated Se compounds (e.g. dimethyl selenone, and dimethylselenonium), if present in solution, are

converted to DMSe (Cooke and Bruland, 1987). In our procedure the produced DMSe is stripped out of the solution and trapped, together with the H_2Se, on the sample trap immersed in liquid N_2. The controlled heating of the sample trap at the end of the analysis resulted in a separation and sequential volatilization of H_2Se and DMSe based on the difference in their boiling points. Due to the efficient separation of H_2Se and DMSe, the detection by AAS resulted in two distinct and sharp peaks: 1) H_2Se from Se(IV) and, 2) DMSe from the reduction of oxidized methylated Se compounds (Figure 3). It is important to note that although this technique allowed for the quantification of simple oxidized methylated Se compounds, the organoselenium compounds present are not specifically identified. Calibration of the instrument using standards of inorganic Se and DMSe enabled specific detection and quantitation of both dissolved Se(IV), and simple oxidized methylated Se compounds.

Determination of dissolved Se(VI), and [Se(0)+Se(-II)]

As in previous published methods (Cutter, 1978; Fio and Fujii, 1990; Yamada and Hattori, 1990), Se(VI) and [Se(0)+Se(-II)] were determined by difference between the Se(IV) and [Se(IV)+Se(VI)], and the [Se(IV)+Se(VI)] and total Se analysis, respectively.
Selenate [Se(VI)] was converted to Se(IV) by acidifying a 20 mL solution containing the standard (or sample aliquot) to 6 M HCl with conc. HCl in a 100 mL beaker. The beaker was covered with a watch glass and the resulting solution heated on a hot plate (at 100 $\pm$ 5 ^{o}C) for 45 min. This resulted in a quantitative reduction of Se(VI) to Se(IV). After the sample was cooled to room temperature, the solution was diluted with

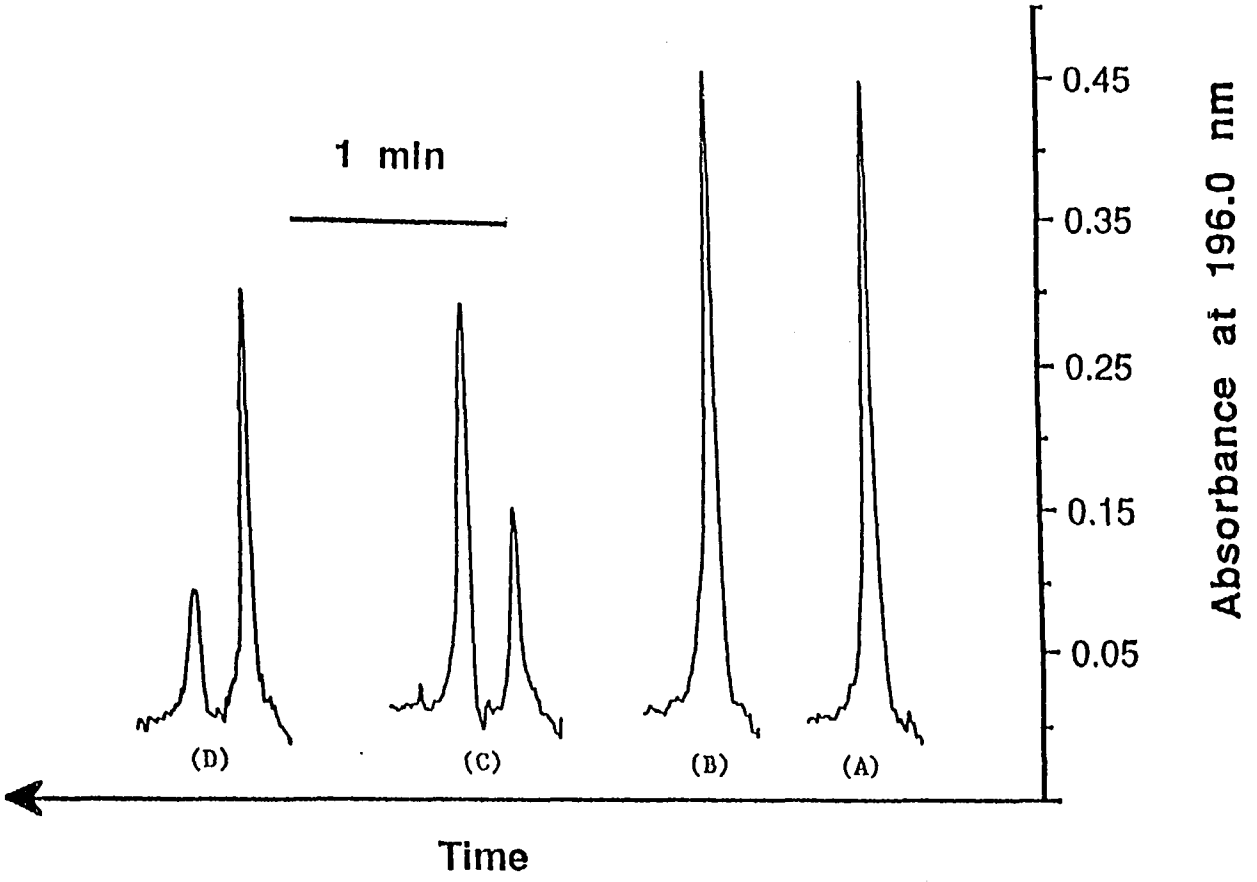

Figure 3: Absorption signals from four consecutive analyses of standards containing: A) and B) 100 ng Se(IV), C) 30 ng Se(IV) and 60 ng DMSe-Se and, D) 60 ng Se(IV) and 15 ng DMSe-Se. Peaks were recorded from right to left.

distilled deionized water to obtain a final matrix of 4 M HCl and analyzed for Se(IV).

Total non volatile Se was determined according to Fio and Fujii (1990). In a first step all dissolved Se species present are oxidized to Se(VI). Then the Se(VI) is reduced to Se(IV) and determined by hydride-AAS. Four mL of a freshly prepared 2.0 % $K_2S_2O_8$ solution and 0.5 mL 4 M HCl are added per 10 mL sample aliquot. If necessary the solution is diluted with distilled deionized water to 20 mL. The resulting solution is digested on a hot plate (at 100 $\pm$ 5 ^{o}C) for 30 min to decompose all organic matter and to convert all dissolved Se compounds to Se(VI). Then 3 mL of a 0.3 % oxalic acid solution per 10 mL sample aliquot is added and the solution is heated for another 15 min.. After cooling to room temperature the solution is further treated as for the [Se(VI)+Se(IV)] determination. The difference between the total Se content and the [Se(VI)+Se(IV)] fraction represents the [Se(0)+Se(-II)] fraction. This fraction includes colloidal elemental Se as well as inorganic and organic Se(-II) compounds.

ANALYTICAL PERFORMANCE OF THE TECHNIQUE

Absorbance was found to be linear over the range 0 - 150 ng of Se (amount placed in the hydride generator) with a sensitivity of 0.0045 absorbance units ng^{-1} of Se. The detection limit, defined as the amount of Se required to give an absorption signal equal to twice the standard deviation of the background signal, was 5 ng Se. Background noise due to flame flickering was found to be the most important factor affecting the detection limit. Up to 50 mL of sample aliquot could be loaded in the hydride generator which allowed for the determination of Se

concentrations as low as 0.1 ng Se mL^{-1} sample. A relative standard deviation of 4.8 % was obtained for six absorbance measurements at the 50 ng level. The above analytical figures of merit were valid for Se derived from Se(IV) as well as from DMSe. Evaluation of the peak area with an integrator would probably have led to better reproducibility.

Triplicate analyses (as total Se) of two EPA water pollution quality control reference samples for Se yielded values of 12.0 $\pm$ 2.1 and 48.6 $\pm$ 4.2 ug L^{-1} compared with the true values of 10.9 and 50.2 ug L^{-1}, respectively.

SELENIUM SPECIATION IN SEDIMENT WATER EXTRACTS

Application of the Se speciation method was tested on sediment-water extracts. Suspensions of selenium contaminated Kesterson Reservoir (CA) and Hyco Reservoir (NC) sediments were centrifuged, and filtered through a 0.45 um micropore filter. The filtered extracts were analyzed for DMSe, Se(IV), oxidized methylated organoselenium compounds, Se(VI), and Se(-II,0). Results are summarized in Table 1. The dominance of Se(VI) and Se(IV) in the Hyco Reservoir sediment extract reflects the oxidized nature of the sediment. In the anaerobic Kesterson Reservoir sediment, Se(0,-II) were the only Se species present. The effect of sediment redox potential on Se speciation and transformations was investigated in detail and will be reported later.

One of the major concerns in analyzing complex sample matrixes is the presence of high concentrations of interfering elements. Metals of groups VIII, especially concentrations of Fe, Co, and Ni exceeding 10 mg L^{-1}, as well as the presence of high concentrations of Pb, Cu, and Sn are reported (Brown et al., 1981; Pierce and Brown, 1977) to interfere

Table 1: Selenium speciation in two sediment-water extracts

Sediment	Redox	SeTot	Se(VI)	Se(IV)	Se(-II,0)	DMSe	Ox.MSe
	(mV)	<----------		µg L^{-1} sediment extract			---------->
Hyco Reservoir	+500	173.4[a] ±51.7[b]	108.1 ±35.8	43.0 ±21.8	3.28 ±0.42	12.5 ±9.57	6.57 ±3.85
Kesterson Reservoir	-200	13.0 ±2.10	ND[c]	ND	13.0 ±2.10	ND	ND

a: Mean of duplicate extracts b: Standard deviation c: Not Detectable

with the hydride generation of Se. Fortunately, the concentrations leading to interelement interferences are generally much higher than those encountered in sediment-water extracts and other natural waters. On the other hand, NO_2 levels as low as 50 ug L^{-1} interfere with the generation of H_2Se (Cutter, 1983). Possible interference of nitrites was eliminated by adding 2 mL of a 2 % (w/v) sulfanilamide solution prior to loading the sample into the hydride generator (Cutter, 1983). To verify the absence of matrix interferences aliquots of sediment extract were spiked with known amounts of both Se(IV) and Se(VI). Satisfactory recoveries (generally between 95 and 100 %) of added Se were obtained.

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CHAPTER II

ARSENIC SPECIATION USING A pH SELECTIVE HYDRIDE GENERATION / SEPARATION TECHNIQUE FOLLOWED BY ATOMIC ABSORPTION SPECTROPHOTOMETRY DETECTION.

ABSTRACT

Based on an investigation of hydride generation responses in solutions of various acidities containing nanogram quantities of arsenite [As(III)], arsenate [As(V)], monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMAA) a sensitive analytical method for the accurate determination of inorganic and organic As species in aqueous solutions was developed. After a pH-selective reduction, the arsenic species were condensed in a U-tube filled with a gas chromatographic packing immersed in liquid N_2. The species were then separated by slow warming of the trap and measured with an atomic absorption spectrophotometer. The arsines from inorganic As(III) were selectively generated from a solution buffered at a pH of 6.0. The solution was then further acidified to a pH corresponding to 2 M HCl and analyzed for As(V). A second sample aliquot, buffered at pH 1.5 with oxalic acid, was used for the quantitative determination of [As(III)+As(V)], MMAA and DMAA.

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INTRODUCTION

Speciation is important in the study of the environmental behavior of arsenic (As) since major features affecting movement and toxicity of As are associated with changes in oxidation states and the resulting differences in chemical properties of these various chemical forms (Brannon and Patrick, 1987; Schroeder and Balassa, 1966; US EPA, 1976; Woolson et al., 1971). The species of special interest include arsenite [(As(III)], arsenate [As(V)], monomethylarsonic acid (MMAA), and dimethylarsinic acid (DMAA).

A pH-selective arsine generation technique followed by atomic absorption spectrophotometry is a popular analytical technique for the determination of inorganic arsenic species (Andreae, 1977; Arbab-Zavar and Howard, 1980; Braman et al. 1977; Glaubig and Goldberg, 1988). However, several researchers, each using their own procedure, came to different conclusions concerning the redox stability of aqueous solutions containing inorganic arsenic species and the time scale on which spontaneous changes in species distribution occurred (Feldman, 1979; Glaublig and Goldberg, 1988; Tallman and Shaikh, 1980;). In order to accurately quantify speciation and obtain reliable information on oxidation-reduction of inorganic arsenic species in the environment, it is necessary to precisely control experimental conditions for arsine generation.

The separation and determination of inorganic As species, MMAA and DMAA based on the sequential volatilization of their hydrides from a liquid nitrogen (LN_2) trap and detection by atomic absorption has been described by several researchers. (Andreae, 1977; Braman et al., 1977;

Howard and Arbab-Zavar, 1981; Shaikh and Tallman, 1978;). Braman et al. (1977) described a technique to separate and quantitatively determine inorganic As, MMAA and DMAA. The arsenicals were reduced to their corresponding arsines and collected on a LN_2 trap. After sequential volatilization the arsines were detected by a recording d.c.-discharge emission scanning monochromator system. The same technique was used by Shaikh and Tallman (1978) and Howard and Arbab-Zavar (1981), but an atomic absorption spectrophotometer was used as the detection system. In these systems the arsine trap was a U-tube half-filled with glass beads.

Andreae (1977) and Johnston (1978) reported that arsines are irreversibly captured by glass beads. Therefore Andreae (1977) used silanized glass wool as packing for the sample trap. A longer open tube was used by Johnston (1978) to trap and separate the arsines. Due to peak broadening and overlap, the above mentioned techniques are limited in their abilty to separate AsH_3 from the methylated arsines, and the methylated arsines from each other. By using a U-tube packed with an appropriate gas chromatographic support as a hydride trap we were able to achieve a better, more efficient and reproducible arsine separation. In this paper we describe the necessary conditions for the accurate speciation between As(III) and As(V) as well as a simple method for the successful separation and determination of trace amounts of organic As compounds in the presence of inorganic As.

MATERIALS AND METHODS

Apparatus

Throughout this study, arsenic species [As(III), As(V), MMAA, and DMAA] were determined using a hydride generation/trapping/separation/ detection apparatus. The system included a helium purged reaction vessel, a glass U-tube immersed in an ice bath, a glass U-tube packed with a gas chromatographic support immersed in liquid nitrogen, and a Perkin-Elmer 360 atomic absorption spectrophotometer (Perkin-Elmer Corp., Norwalk, CT) fitted with a flame-in-tube burner. Figure 1 shows the apparatus used for the generation, trapping, and separation of the arsines. The reaction vessel, a gas washing bottle, could hold up to 75 mL. Reagents were added through a rubber septum. The helium carrier gas (150 mL min^{-1}) entered the reaction vessel through a fritted glass bubbler. A pyrex U-tube (length, 30 cm; i.d., 4 mm) immersed in an ice bath was found to be effective in removing water vapor form the gas stream before it reached the sample trap. If this drying tube was ommited, the liquid nitrogen arsine trap became quickly clogged with ice. The arsine trap consisted of a 40-cm pyrex U-tube (4 mm i.d.) filled with a 10 % SE-30 packing on 80/100 Supelcoport (Supelco, Inc., Bellefonte, PA). The tube was wrapped with 1.5 m of 1 mm Nichrome wire (Sargent-Welch, Skokie, IL). The wire, connected to a variable transformer with alligator clips, acted as heating element. Connections between the reaction vessel, the water, and arsine trap were made with Tygon tubing (Nalge Compagny, Rochester, NY). The outlet of the arsine trap was connected to the auxiliary input of a quartz flame-in-tube burner with Teflon tubing.

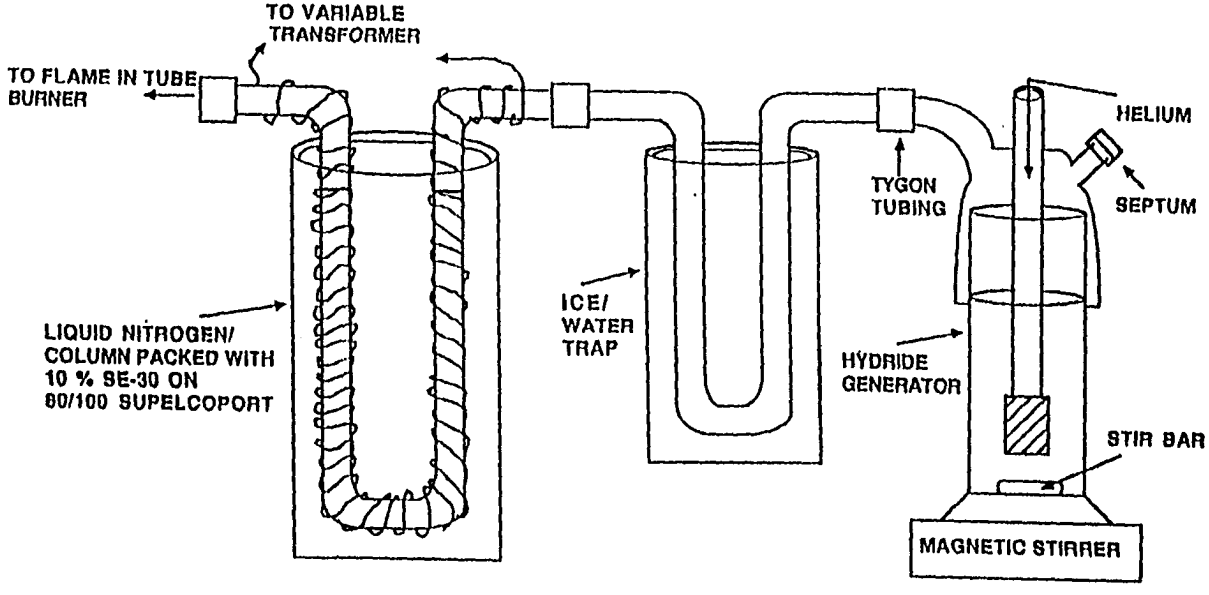

Figure 1: Apparatus for the generation, trapping, and separation of arsines.

The stainless steel burner mount and quartz cell (Fig. 2) were custom made after a design originally described by Johnston (1978). The quartz cell (length, 12 cm; i.d., 12 mm) burned an air-hydrogen flame (H_2 flow, 280 mL min^{-1}; air flow, 150 mL min^{-1}) and was aligned in the optical beam path of the atomic absorption spectrophotometer. A hollow cathode lamp (lamp current, 8 mA) was used as a light source and absorbance was measured at 197.3 nm. Instrument settings for the atomic absorption spectrophotometer were: slitwidth, 0.7 nm; gain setting, 50%; and mode, TC1. The output was recorded on a strip chart recorder and peak heights were used to calculate concentrations.

Standards and Reagents

MMAA, DMAA, arsenite and arsenate stock solutions were prepared from their sodium salts. Standard solutions containing 100 ug As L^{-1} were diluted daily from intermediate stock solutions containing 10 mg As L^{-1}. To assure that no As(III) contamination was present the 10 mg L^{-1} As(V) stock solutions were oxidized by boiling in 5% HNO_3 before diluting (Glaubig and Goldberg, 1988). Ascorbic acid added to the As(III) standards prevented the oxidation of As(III) to As(V) (Feldman, 1979). The As content of the MMAA and DMAA standards were verified using a Jarrel Ash (Atom Comp Series 800, Waltham, MA) ICP. The purity of the organic arsenicals was checked using a hydride/generation/separation technique (described later). No further purification of the standards was neccesary.

A range of pH buffers from 1.5 to 8.0 was prepared in a following manner. Tris buffer solutions (pH 8.0, 7.0 and 6.0) were prepared by treating a 2 M solution of Trizma Base [tris (hydroxymethyl)

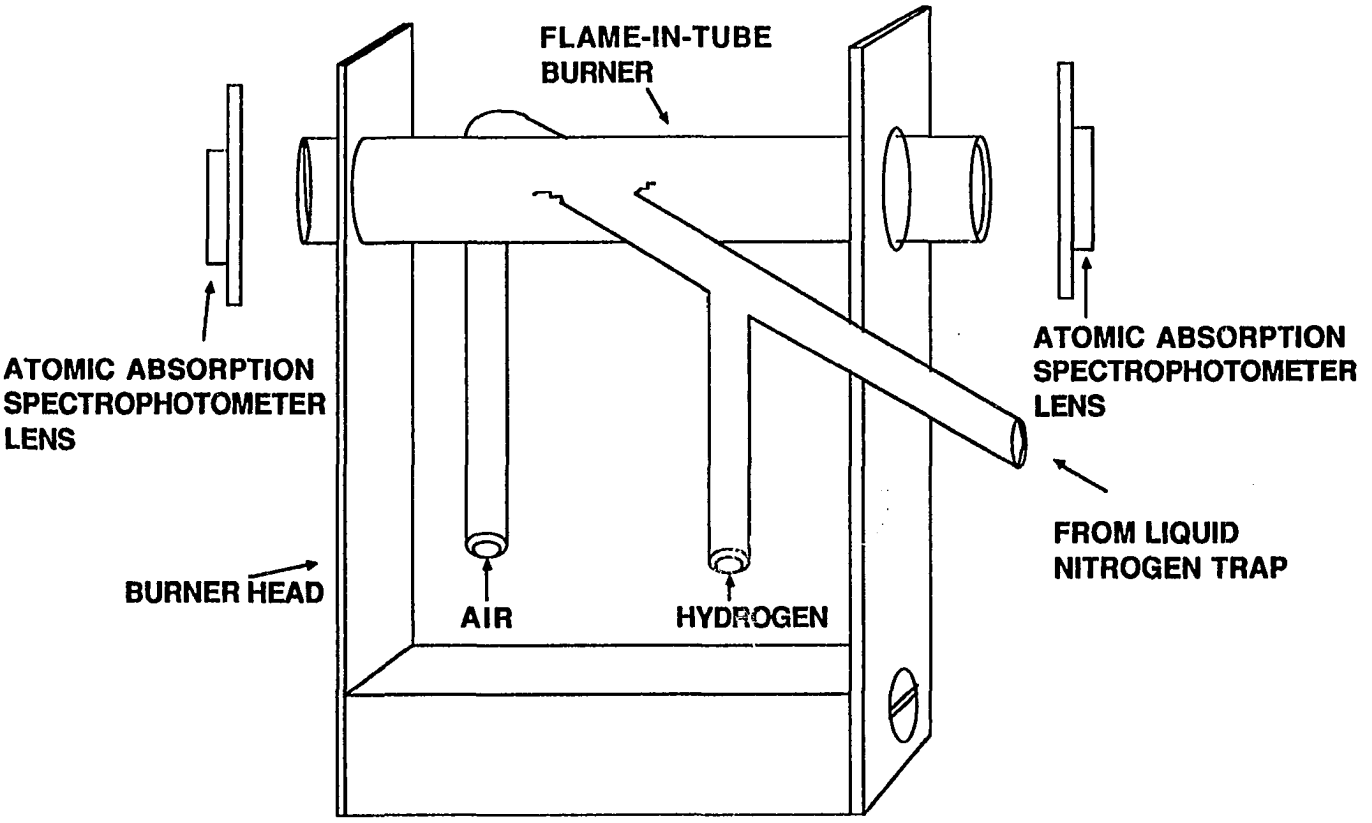

Figure 2: Flame-in-tube burner used for Atomic Absorption Spectrophotometry detection of arsines.

aminomethane] with sufficient 4 M HCl until the desired pH was obtained. Buffers of pH 5.0 and 4.0 were obtained by acidification (with 4 M HCl) of a solution containing 2 M sodium citrate. A 10 % oxalic acid solution was used to buffer the solutions at a pH of 1.5. Other acidities used in this study were prepared by diluting the appropriate amount of concentrated HCl. All chemicals listed above and the $NaBH_4$ used to generate the arsines were analytical grade. The analytical grade HCl contained a small amount of As (1.56 ng As mL^{-1} conc. HCl). To avoid this problem ultrapure HCl could be used. The other chemicals had As levels below our detection limit (2 ng As). Due to the alkaline nature of the $NaBH_4$ the pH of the solution tended to increase during the addition of the reducing agent. Each mixture was therefore tested for its buffering capacity. Buffers of 0.2 M concentration limited pH increases to 0.5 units after addition of $NaBH_4$, and were therefore used throughout this study.

Analytical procedure

Forty five milliliters of distilled deionized H_2O, 5 mL of the appropriate buffer solution and the As standard were added to the hydride generator. The system was flushed with helium and the arsine trap was immersed into liquid nitrogen (LN_2). After cooling, 4 mL of 3 % $NaBH_4$ was injected (4 mL min^{-1}) through a septum into the reaction vessel, while continuously stripping with helium. After 7 min, the inorganic As(III), As(V), MMAA, and DMAA were reduced to their corresponding arsines, swept out of the solution, and trapped on the sample trap immersed in LN_2. After removing the LN_2, the trap was slowly heated by means of the Nichrome wire wrapped around the trap and

connected to a variable transformer. This slow warming of the trap resulted in a sequential volatilization of the arsines based on their boiling points. The detection of the arsines by atomic absorption spectrophotometry resulted in three distinct and sharp peaks: 1) AsH_3 from the reduction of As(III) or As(V), 2) CH_3AsH_2 (MMA) from the reduction of MMAA, and 3) $(CH_3)_2AsH$ (DMA) from the reduction of DMAA. With the gas chromatographic support and a U-tube temperature ramp produced with an autotransformer setting of 12 V, the volatilization times were 26, 51, and 68 s for AsH_3, MMA and DMA, respectively.

RESULTS AND DISCUSSION

Analytical Method Performance Characteristics

The performance of hydride generation, cryogenic condensation and volatilization followed by atomic absorption detection was assessed by analysis of laboratory standards of As(III) and EPA water pollution quality control reference samples. Absorbance was found to be linear over the range 2 - 120 ng As. The sensitivity was 0.0083 absorbance units/ng of As. A relative standard deviation of 2.3 % was obtained for six absorbance measurements at the 50 ng level. The detection limit, defined as the amount of As required to give an absorption equal to twice the standard deviation of the background signal, was 2 ng As. Up to 75 mL of solution can be loaded into the reaction vessel which makes it possible to detect As concentrations as low as 0.026 ng mL^{-1} solution. Background noise due to flame flickering was found to be the most important factor affecting the detection limit in our system. Analysis (in 4 M HCl) of two EPA reference standards for total inorganic

As [As(III) + As(V)] yielded values of 25 ± 1.2 and 241 ± 15 ug L^{-1} (n=4) compared with the true values of 26.7 and 235 ug L^{-1}.

Inorganic arsenic speciation procedure

It has been well documented that selective reduction of inorganic As(III) and As(V) species can be controlled by pH adjustment. Selective volatilization of As(III) has been accomplished at a pH of 4.0 to 5.0 (Glaubig and Golberg, 1988; Howard and Arbab-Zavar, 1981; Shaikh and Tallman, 1978) and at pH of about 6.0 (Andreae, 1977; Johnston, 1978) to 7 (Brannon and Patrick, 1987). Figure 3 summarizes the effect of pH on the evolution of arsine from aqueous solutions containing 50 ng As(III), As(V), MMAA or DMAA using the previously described apparatus and analytical procedure. While the hydride generation from As(III) is essentially independent of the pH, the amount of arsines released from As(V), MMAA and DMAA is clearly pH sensitive. In acidities corresponding to 2 M HCl and greater, inorganic As(III) and As(V) responded similarly in our system. Arsines generated from a solution buffered at a pH of 6 to 7 were solely from As(III). At a pH of 5.0 we noted a 3 % volatilization of 50 ng of As(V). Since both inorganic As species yield the same hydride, it is necessary to buffer the solution at a pH of 6.0 or 7.0 to determine As(III). After analyzing for As(III) the solution can be acidified to make a 2 to 6 M HCl solution and the As(V) species can be quantitatively determined. The increase in sample volume caused by the addition of the HCl (15 mL in our experiments) did not effect the efficiency of arsine generation.

When the $NaBH_4$ volume was increased from 4 to 10 mL, it was also possible to quantitatively determine As(V) in a solution buffered at pH

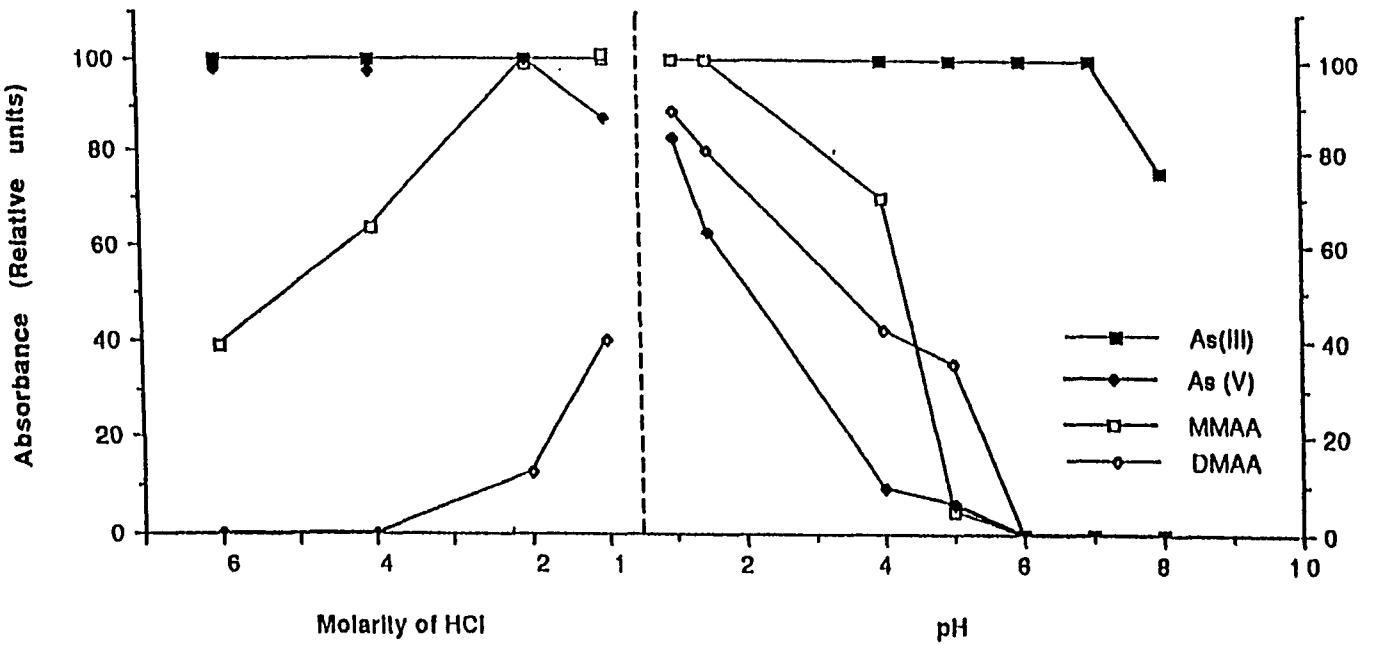

Figure 3: Effect of hydride generator acidity on arsine absorption signal (50 ng As, 4 mL of 3% $NaBH_4$).

1.5 (by adding 10 mL of 10 % oxalic acid solution). However, in our experiments the absorbance for As(V) was never quantitative when oxalic acid was used to lower the pH after analysing for As(III), although this procedure has been suggested (Andreae, 1977; Johnston 1978). When oxalic acid was added, after buffering at pH 6 and analyzing for As(III), the pH of the solution dropped to 2.8 and the absorbance of 50 ng As(V) reached only 38 % of its value compared to when HCl was used (Fig.3). Increasing the $NaBH_4$ volume from 4 to 10 mL only volatilized 93±4 % (n=6) of the As(V) present.

The accurate determination of inorganic As species was not only a function of the pH chosen for the selective volatilization but was also dependent on the concentration of the different species present. When the solution was buffered at pH between 6.0 and 7.0, the accurate determination of As(III) was succesfully accomplished in the presence of 200 ng As(V) (Fig.4). In the presence of greater concentrations of As(V), dilution was necessary. It is possible to accurately determine As(III) from a solution with a As(III) / As(V) ratio of 1/100 (detection limit of 2 ng As).

Determination of MMAA and DMAA

The absorbance obtained for 50 ng of spiked DMAA from HCl (1M and greater) was found to be 40 % or less compared to the response of an equal amount of inorganic As. At acidities greater than 2 M HCl the absorption signal for MMAA was no longer quantitative (Fig.3). Therefore the analysis of MMAA and DMAA was conducted after buffering the solution at a pH of 1.5 by adding 10 mL of 10 % oxalic acid. In order to achieve a quantitative absorption signal from As(V) and DMAA, 10 mL of 3% $NaBH_4$

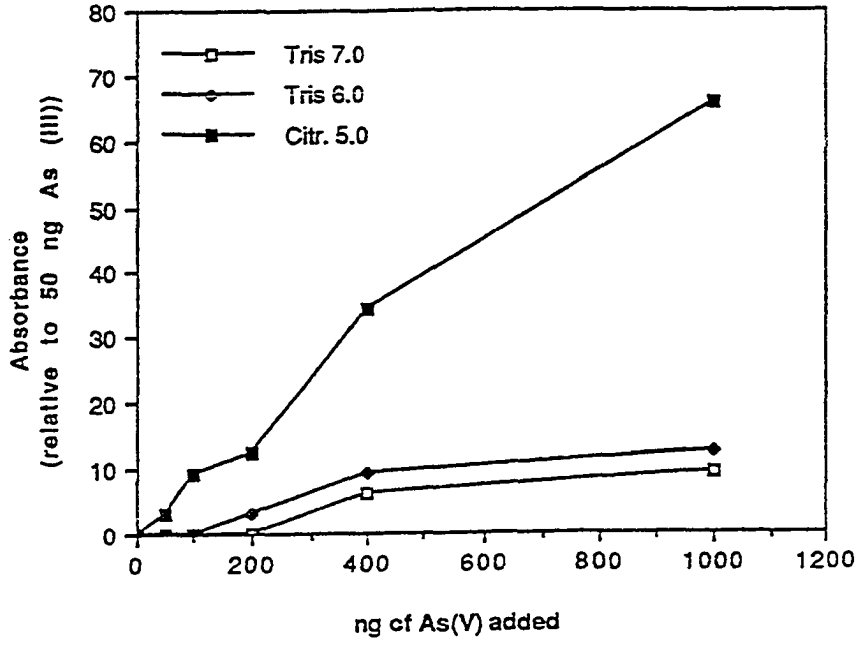

Figure 4: Interference of As(V) in As(III) determinations at three pH values.

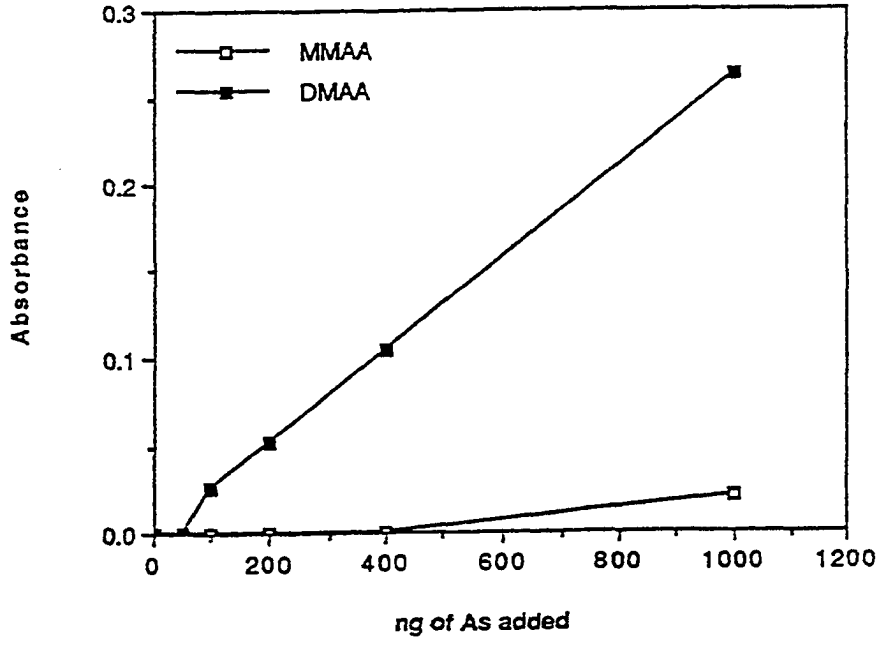

Figure 5: Absorption signal from monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMAA) as a function of concentration at pH 6.

was added and the stripping time was increased to 8 min. Under these conditions the organic arsenicals could be determined with the same sensitivity and detection limit as the inorganic As species. No methylation or demethylation of MMAA and DMAA were noted at this pH, which confirms the work of previous authors (Braman et al., 1977; Talmi and Bostick, 1975).

Figure 5 illustrates the volatilization of MMA and DMA from solutions containing increasing amounts of MMAA or DMAA in the pH 6.0 solution used to generate the AsH_3 from As(III). The volatilization of the methylated arsines does not influence the absorbance obtained for AsH_3 in the analysis of As(III), but if the organic arsenicals were in concentrations greater that 100 ng significant losses of organic arsenicals occurred during the analysis of As(III). It therefore was necessary to use a second sample aliquot for the determination of MMAA and DMAA in solution.

Most commercially available systems and the commonly used continuous flow hydride-generation apparatus (Glaubig and Goldberg, 1988) are not able to separate inorganic from organic As compounds. Therefore they are limited in their ability to obtain a correct speciation of As. In the presence of MMAA and/or DMAA, As(III) or As(V) will be overestimated. The error will be function of the pH values chosen for the selective volatilisation of the inorganic As species and of the amount of organic arsenicals present (Fig.3 and 5). Brannon and Patrick (1987) inserted a H_2SO_4 trap between the hydride generator and the atomic absorption spectrophotometer to separate alkylarsines from inorganic arsines. While AsH_3 passed through the H_2SO_4 trap, the

alkylarsenicals were trapped. Although this trap was efficient in separating alkylarsines from inorganic arsines in samples containing 10 - 100 ug L^{-1} of inorganic and organic As, this technique does not allow for the identification of the organic arsenicals present.

Arsenic speciation in natural samples

Table 1 shows the As(III), As(V), [As(III) + As(V)], MMAA, and DMAA concentrations and recoveries of selected sample solutions spiked with 10 and 50 ng of the different As species. Samples analyzed for this study were: 1) Mississippi river water, collected at Baton Rouge (La), 2) a deionized water extract (soil/water = 1/5) of a Crowley soil (Typic Albaqualf), and 3) a porewater extracted by centrifugation and filtration from an anaerobic sediment (Hyco Reservoir, NC). The arsines from inorganic As(III) were selectively generated from a solution buffered at a pH of 6.0. Following the As(III) analysis the sample was acidified to a pH corresponding to 2 M HCl and further analyzed for As(V). A second sample aliquot, buffered at a pH 1.5 with oxalic acid, was used for the quantitative determination of [As(III)+As(V)], MMAA and DMAA. Relative standard deviations of these analyses (n=3) were 5.0 % or less. Recoveries of added As species were within 6.0 % of the expected values. The amount of inorganic As determined as the [As(III)+As(V)] fraction was equal ($\pm$ 6.0 %) to the sum of the As(III) and As(V) analysis. Methylated As species were only present in the porewaters of the anaerobic sediment.

Interference effects have been thoroughly studied for the hydride generation of As. Concentrations of Co, Ni, Sn and Pb greater than

Table 1: Arsenic concentrations and recoveries of spiked sample solutions

Sample	Additions of arsenic standards				arsenic determined				
	As(III)	As(V)	MMAA	DMAA	As(III)	As(V)	As(III+V)	MMAA	DMAA
	<---------- ng mL $^{-1}$ ----------				---------->				
Mississippi river water	0	0	0	0	0.97	10.5	12.0	ND*	ND
	10.0	10.0	10.0	10.0	11.0	22.0	33.5	10.0	10.0
	50.0	50.0	50.0	50.0	52.0	61.0	110	49.0	49.5
Crowley soil extract	0	0	0	0	7.50	15.0	24.0	ND	ND
	10.0	10.0	10.0	10.0	19.0	23.5	45.0	10.0	10.5
	50.0	50.0	50.0	50.0	55.0	63.0	126	53.0	52.0
Hyco Reservoir sediment porewater	0	0	0	0	105	14.0	119	ND	7.0
	10.0	10.0	10.0	10.0	116	23.0	142	9.5	17.0
	50.0	50.0	50.0	50.0	159	65.6	230	48.0	59.0

*: ND = Not detectable in a 5 mL sample

1 mg L^{-1} and nitrite are reported to be the most important interferents (Brown et al., 1981; Pierce and Brown, 1977). The data in Table 1 indicate that arsine generation was not influenced by matrix interferences in the samples analyzed and illustrate the capability of the analytical technique in determining As speciation in natural samples. Due to the high sensitivity and low detection limit of the described analytical technique a small sample volume (usually 1.0 mL or less) is required for the analysis. The use of small sample volumes reduces the concentration of possible interfering substances.

SUMMARY AND CONCLUSION

A sensitive analytical technique for the accurate determination of the As species commonly encountered in the environment is reported. After reduction, the arsenic species are condensed in a U-tube, filled with a gas chromatographic packing, immersed in a LN_2 trap. The species were then separated by slowly warming the trap and As measured by atomic absorption spectrophotometry. The use of a gas chromatographic packing led to a better, more efficient and reproducible arsine separation as compared to previous published methods. The arsines from inorganic As(III) are selectively generated from a solution buffered at a pH of 6.0. Following the As(III) analysis the sample is acidified to a pH corresponding to 2 M HCl and further analyzed for As(V). A second sample aliquot, buffered at a pH 1.5 with oxalic acid, is used for the quantitative determination of [As(III)+As(V)], MMAA and DMAA.

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CHAPTER III

SPECIATION AND REDOX CHEMISTRY OF SELENIUM IN KESTERSON RESERVOIR (CA) SEDIMENTS.

ABSTRACT

The influence of redox potential and pH on selenium solubility, speciation, and volatilization was studied. Kesterson Reservoir sediments contaminated with selenium were incubated under controlled redox (-200, 0, 200, and 450 mV) and pH (6.5, natural, 8.5, and 9) conditions. Under reduced conditions selenium solubility was low and controlled by an iron selenide phase. Se(-II,0) comprised 80-100% of the total soluble selenium. Upon oxidation dissolved selenium concentrations increased. The oxidation of Se(-II,0) to selenite was rapid and occurred immediately after the oxidation of iron. Above 200 mV selenite slowly oxidized to selenate. Under oxidized conditions (450 mV) selenium solubility reached a maximum. Selenate was the predominant dissolved species present, constituting 95% at higher pH's (8.5, 9) to 75% at lower pH's (7.5, 6.5) of the total soluble selenium at 450 mV. Biomethylation of selenium occurred only under oxidized conditions. Redox potential and pH are key factors in the biogeochemistry of selenium.

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INTRODUCTION

The discovery of toxic concentrations of selenium (Se) in evaporation ponds of the Kesterson National Wildlife Refuge, located in the Western part of California's San Joaquin Valley, has led to an increasing interest in the biogeochemistry of selenium in recent years.

The chemistry of selenium is complicated since it can exist in four different oxidation states: selenide (Se(-II)), elemental Se (Se(0)), selenite (Se(IV)), and selenate (Se(VI)), and as a variety of organic compounds. The major features of selenium biogeochemistry affecting its movement and toxicity are associated with changes in its oxidation state and the resulting differences in chemical properties of these various chemical forms. Adsorption and mobility of the selenite and selenate species have been studied extensively during the past few years (Ahlrichs et al., 1987; Alemi et al., 1988a, b; Balistrieri and Chao, 1987; Bar-Yosef and Meek, 1987; Neal et al., 1987a, b). Briefly, conditions that favor the mobility of selenium with respect to adsorption are alkaline pH, oxidizing conditions, and high concentrations of additional anions.

Although the importance of the redox status in the study of selenium biogeochemistry is evident, few studies have investigated the effects of changes in oxidation-reduction potential on the transformations of selenium species in soils and sediments. Geering et al. (1968) constructed an Eh-pH diagram and theoretically investigated selenium transformations as affected by pH and Eh. In a more recent paper, Elrashidi et al. (1987) used thermodynamic data to develop equilibria reactions and constants for selenium minerals and solution species that relate to soils. Based upon thermodynamics, they reported

metal-selenite and in particular metal-selenate minerals to be too soluble to persist in soils. At low redox potentials however, elemental Se or a metal-selenide could control Se solubility.

We developed a laboratory experiment that allowed us to study selenium transformations under controlled redox and pH conditions. In this paper we describe the critical redox levels at which selenium transformations in contaminated Kesterson Reservoir sediments occurred and report the influence of redox and pH on selenium speciation, solubility, and volatilization.

MATERIALS AND METHODS

Sediments

Selenium contaminated sediments of the Kesterson Reservoir in California were collected at the northeast side of pond #2, approximately 30 m from the levee. The sediment was transported to the laboratory in tightly closed plastic containers.
Upon arrival the sediments were homogenized under an argon atmosphere and stored in closed 4-L polyethylene flasks until use.

Incubation apparatus

The sediments were incubated in laboratory microcosms at various redox-pH conditions by using a modification of the redox control system developed by Patrick et al. (1973) (Figure 1). In this system, the suspension pH is continuously measured and manually adjusted by additions of 4 M HCl or NaOH, daily, or as required to bring the pH to the desired value. The redox potential was maintained at a preselected potential automatically. Platinum electrodes in the suspension were

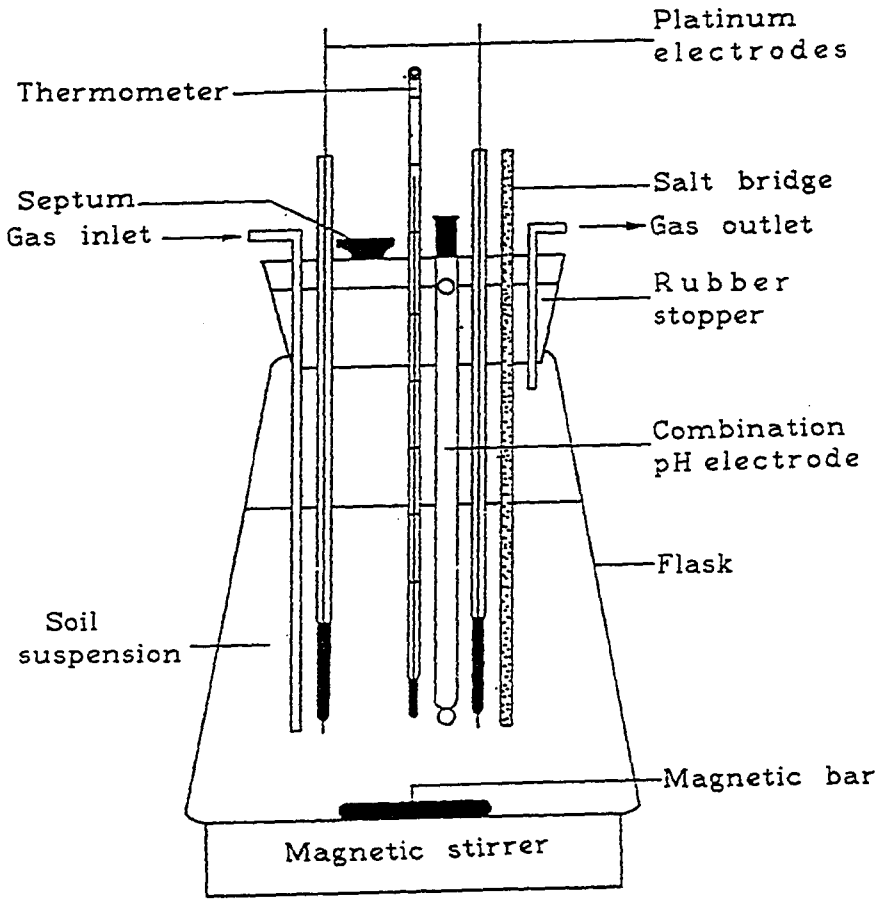


Figure 1: Schematic of experimental setup used for pH and redox control of the sediment suspensions.

connected to a millivolt meter to give continuous measurement of the redox potential of the sediment-water suspension. The recorder output of the millivolt meter was in turn connected to a meter relay that activated an air pump. Whenever the redox potential dropped below the desired potential, a small amount of air was pumped into the system to maintain the desired redox potential. This system of regulating redox potential with air input works because, in the absence of oxygen, chemical and especially microbial processes cause the redox potential to decrease. The flasks were continuously purged with oxygen-free argon gas. Argon gas was effective in purging excess air at the end of the aeration cycle and in preventing a buildup of gaseous decomposition products such as carbon dioxide and hydrogen sulfide. Using this system, we could maintain the desired redox potential within $\pm$ 20 mV. The outflow gas passed out the incubation apparatus into a 10-mL concentrated HNO_3 solution followed by a water trap. Nitric acid has been reported to retain volatile selenium compounds from soils (Abu-Erreish et al., 1968).

Experiments

In experiment one, the critical redox levels where selenium transformations occur were determined. Suspensions of the strongly reduced sediments were incubated (at 28 $\pm$ 2 ^{o}C) in the microcosms for 6 h before adjusting redox levels. Suspensions were prepared by mixing an amount of sediment equivalent to 200 g of dry weight with distilled water so that the final sediment water ratio was 1 to 7. Four incubations were performed each at a different Eh; -200, 0, 200, and 450 mV. The experiment was run in duplicate. The microcosms were sampled at

5-day intervals over a 3 week period. The pH was monitored and recorded.

In experiment two, similar sediment suspensions were equilibrated under controlled redox and pH conditions. The following redox-pH combinations were used: redox -200, 0, 200, and 450 mV; pH 6.5, natural, 8.5, and 9. Natural (uncontrolled) pH values after a 28 day incubation period were 7.5 for 450 mV, 7.8 for 200 mV, 7.9 for 0 mV, and 8.1 for -200 mV. Microcosms were sampled after 28 days of incubation. Incubations were run in duplicate.

A sediment suspension aliquot was withdrawn, centrifuged [20 min at 7000 rpm, Sorvall GSA-400 rotor, DuPont CO., Wilmington, DE] and filtered through a 0.45 uM micropore filter, under an inert argon atmosphere for reduced treatments (Patrick and Henderson, 1981). Five dissolved selenium species were identified in the water extract.

In order to better validate Eh measurements in the systems we also measured the NO_3/NH_4, soluble Mn (Mn(II)), soluble Fe (Fe(II)), and the SO_4/S redox species. Other major cations (Ca, Mg, K, Na, Al), metals (Cu, Zn, Cd, Pb, and Ni), and chlorides were also determined.

Analysis

Selenium species (Se(IV), Se(VI), Se(-II,0), dimethyl selenide (DMSe), and oxidized methylated Se compounds (Ox.MSe)) in the water extracts were determined with a hydride generation/trapping/detection apparatus. The system included a helium purged glass hydride vessel, a glass U tube immersed in an ice bath, a glass U tube immersed in liquid nitrogen, and an atomic absorption spectrophotometer (AAS, Perkin Elmer 360) fitted with a flame in tube burner. The output was recorded on a

strip chart recorder and peak heights were used to calculate concentrations. Absorbance was found to be linear over the range 0-150 ng of selenium (amount placed in the hydride generator) with a sensitivity of 0.0045 absorbance units ng^{-1} of Se and a detection limit of 5 ng of Se.

Extracts were analyzed for selenium species within 10 hours after sampling. A 10-mL aliquot of the extract was purged with He for the determination of volatile dimethyl selenide (DMSe). Dimethyl selenide was trapped on the U-tube immersed in liquid N_2. After controlled heating of the sample trap, DMSe was quantified in a quartz flame-in-tube atomizer aligned in the optical path of an AAS. Aliquots that had been previously stripped of volatile methylated compounds were then analyzed for selenite and dissolved oxidized methylated selenium compounds. Selenite and oxidized methylated Se-compounds were reduced with $NaBH_4$ to H_2Se and DMSe (Cooke and Bruland, 1987), respectively. Entrained by the He carrier gas they were trapped in a liquid N_2 cooled U-tube. Hydrogen selenide and DMSe were separated by controlled heating of the sample trap. They were carried out of the trap into the atomization cell and detected as two distinct and sharp absorption signals. Other aliquots were analyzed for (selenate + selenite), after reduction of Se(VI) to Se(IV) in 6 N HCl (Brimmer et al., 1987); and for total selenium by a modification (Fujii et al., 1988) of the method described by Presser and Barnes (1984). Sulfanilamide was used to eliminate possible nitrite interference in the determination of selenium (Cutter, 1983). The selenate was calculated as the difference between the (selenate + selenite) and the selenite analysis. The difference between the total Se content and the (selenate + selenite) fraction is

the Se(-II,0) fraction. The maximum sample volume analyzed for inorganic selenium species was 5 mL, which gave a detection limit of 1 ug of Se L^{-1} or 7 ug of Se kg^{-1} of dry sediment. Due to the small sample volume analyzed (normally between 0.5 and 2 mL) no interferences in the analysis of selenium species by dissolved organic carbon (Fujii et al., 1988; Roden and Tallman, 1982) were found. Several samples were analyzed by the standard addition technique. The relative precision of the technique was 5% for selenium species that were determined directly and about 10% for the species determined by difference. For the quantification of the volatilized selenium compounds, the HNO_3 solutions were carefully taken to near dryness, 40 mL of 4 M HCl was added and the solutions were treated as for (selenite + selenate) analysis.

Ammonium and nitrate were determined by the Kjeldahl distillation technique. Metals and major cations in solution were analyzed with an Jarrel Ash ICP, and a Dionex Ion Chromatograph was used for chloride and sulfate analysis. EPA reference standards were analyzed to check the preformance of the ICP. Sulfide was measured by an ion-specific Ag/S electrode in an anoxic buffer solution (sulfide electrode operating instructions, Lazar Research Laboratories, Los Angeles, CA). Due to the limited sensitivity of the electrodes, these analyses are probably less accurate.

Total Se in the sediment was determined by the prewetting digestion procedure as described by Fujii et al. (1988).

The loss on ignition method (Davis, 1974) was used to estimate the organic matter content of the sediment.

X-ray diffraction (CuK_α radiation) of bulk powder samples was used to study the mineralogy of reduced and oxidized sediment.

RESULTS AND DISCUSSION

Critical redox potentials for selenium transformations

The sediments from the Kesterson Reservoir were extensively anaerobic and characterized by a high pH (8.1), an organic matter content of 5.2 %, and a dark grayish color due to the large concentration of iron monosulfides. Presser and Barnes (1984) reported the presence of thenardite (Na_2SO_4) in Kesterson reservoir sediments. Our X-ray diffraction patterns showed the presence of a large amount of calcite and some pyrite in the reduced sediments. The sediment had a total Se content of 9.06 $\pm$ 2.40 mg kg^{-1} (n=8) of dry sediment.

The critical redox potentials at which selenium transformations occurred were determined (experiment one). Results from a 3-week incubation study at -200 mV (pe = Eh / 59.16) and 0 mV are given in Tables 1 and 2. When incubated at -200 mV (pH 8.1), the solubility of selenium was very low and Se(-II,0) was the only detectable form (Table 1). At -200 mV nitrogen, manganese, and iron were present in a reduced form. Sulfide concentrations up to 74 mg kg^{-1} of dry sediment were measured. High chloride, sodium, and sulfate concentrations (approximately 4200, 3750, and 3400 mg kg^{-1} of dry sediment, respectively) were due to the solubility of salts like Na_2SO_4 and NaCl. As the incubation time progressed, concentrations of dissolved Na and Cl remained constant in both reduced and oxidized experiments, suggesting the independence of their solubility from oxidation-reduction reactions. Soluble Cu, Zn, Cd, Pb, and Ni were less than 1 mg kg^{-1} of dry sediment.

Oxidation of Se(-II,0) to Se(IV) occurred at an Eh of approximately 0 mV (Table 2). For the first 14 days total soluble selenium

Table 1: Concentration of soluble redox species, and Ca during a 20 day incubation period at -200 mV

Day	NH_4-N	NO_3-N	Mn	Fe	S(-II)	SO_4-S	Ca	Se(-II,0)	Se(IV)
	<----------	mg kg^{-1}	dry	sediment	---------->			<----- µg kg^{-1}	--->
2	212[a] ±11[b]	<2.00[c]	5.74 ±0.20	7.73 ±0.67	65 ±9	2905 ±770	934 ±229	21 ±7	<7[c]
7	241 ±3	<2.00	4.22 ±1.48	7.90 ±1.68	74 ±20	2919 ±697	903 ±168	56 ±28	<7
12	264 ±12	<2.00	5.47 ±0.56	7.95 ±1.72	64 ±20	3052 ±546	931 ±204	42 ±23	<7
20	259 ±6	<2.00	4.55 ±1.32	7.85 ±0.76	70 ±22	3395 ±1021	1091 ±165	84 ±15	<7

a: Mean of duplicate incubations b: Standard deviation c: Detection limit

Table 2: Concentration of soluble redox species, and Ca during a 20 day incubation period at 0 mV

Day	NH_4-N	NO_3-N	Mn	Fe	S(-II)	SO_4-S	Ca	Se(-II,0)	Se(IV)
	<----------	mg kg^{-1} dry sediment			---------->			<----- µg kg^{-1}	--->
2	258[a] ±8[b]	<2.00[c]	4.22 ±0.37	7.95 ±1.01	50 ±3	3402 ±98	1068 ±230	44 ±10	<7[c]
7	229 ±9	<2.00	4.23 ±1.34	6.90 ±1.71	42 ±15	3556 ±826	1165 ±285	42 ±2	<7
12	246 ±12	<2.00	5.18 ±1.57	8.00 ±1.90	45 ±15	3801 ±714	1400 ±290	72 ±14	<7
20	259 ±26	<2.00	7.21 ±0.82	0.55 ±0.25	3 ±3	5056 ±1174	2305 ±475	35 ±7	259 ±103

a: Mean of duplicate incubations b: Standard deviation c: Detection limit

concentrations and forms at 0 mV (pH 7.9) were comparable with those reported for the incubation at -200 mV. However, after approximately 2 weeks the color of the suspension changed gradually from dark grayish to light brown due to the formation of iron oxides. Levels of dissolved iron and sulfides decreased and the sulfate concentration increased sharply illustrating the oxidation of the iron sulfides. The concurrent increase of the calcium concentration (Table 2) is somewhat ambiguous. It could result from the dissolution of gypsum ($CaSO_4.2H_2O$) or anhydrite ($CaSO_4$),

$$CaSO_4.2H_2O = Ca^{2+} + SO_4^{2-} + 2H_2O \qquad (1)$$

or it could result from the oxidation of an ironsulfide (pyrite or an iron monosulfide) and reaction with calcite:

$$FeS_2 + 3.75O_2 + 3.5H_2O = Fe(OH)_3 + 4H^+ + 2SO_4^{2-} \qquad (2)$$

$$4H^+ + 2CaCO_3 = 2Ca^{2+} + 2H_2CO_3 \qquad (3)$$

It is very difficult to distinguish [except perhaps by study of sulfur isotopes (Drever, 1988)] between these alternatives without investigation of the solid phases involved. Mineral identification by X-ray diffraction clearly showed the absence of gypsum and the presence of large amounts of both iron sulfides and calcite in the reduced sediments. Therefore the reactions described in eq (2) and (3) are responsible for the increase of Ca concentration in our experiments. A large part of the alkalinity formed is lost to the atmosphere as CO_2.

Analysis of variance [PROC GLM procedure of the Statistical Analysis System (1985)], comparing the solubility of redox species and calcium at -200 mV to 0 mV support the interpretations made above. Concentrations of soluble redox species and Ca were not significantly different between the two redox levels studied. However, significant

($P<0.05$) differences were found for the dissolved concentrations of Fe, S(-II), Ca, and Se(IV) between the different sampling times. There also was a significant interaction ($P<0.05$) between the days after incubation and the Eh for these elements. As can be implied from Tables 1 and 2, the interaction (day 20, -200 vs 0 mV) can be interpreted as the oxidation of iron sulfides, the consequent release and oxidation of Se(-II,0) to selenite, and the reactions described in eq (2) and (3).

The dominant selenium species found at 200 mV and 450 mV are shown in Figure 2. The transformation of selenite to selenate began at a redox potential of approximately 200 mV (pH was 7.7 at end of incubation) and occurred at values corresponding with nitrification and denitrification. Low concentrations of dissolved Mn (0.17 ± 0.08 mg kg^{-1}), Fe (0.87 ± 0.36 mg kg^{-1}), and S(-II) (< 0.02 mg kg^{-1}) were typical for the oxidized sediment. Concentrations of Ca and SO_4-S at the end of the incubation period were 2710 ± 212 and 4780 ± 590 mg kg^{-1} dry sediment, respectively. When incubated at 450 mV, the oxidation of ammonium to nitrate and selenite to selenate was evident after 2 days of incubation (Figure 2B). Over time almost all selenite was oxidized and selenate became the dominant selenium species in solution. At the end of the incubation the dissolved concentrations of the other redox species (mg kg^{-1} of dry sediment) were as follows: Mn, 0.08 ± 0.05; Fe, 0.61 ± 0.48 ; S(-II), < 0.02. During the incubation the pH dropped from 8.1 to 7.5 and soluble SO_4-S and Ca concentrations rose to 5159 ± 903 and 3160 ± 480 mg kg^{-1}, respectively.

Figure 3 summarizes the order of various inorganic oxidation-reduction reactions for the Kesterson Reservoir sediments. Data presented indicate that the oxidation and chemical weathering of iron

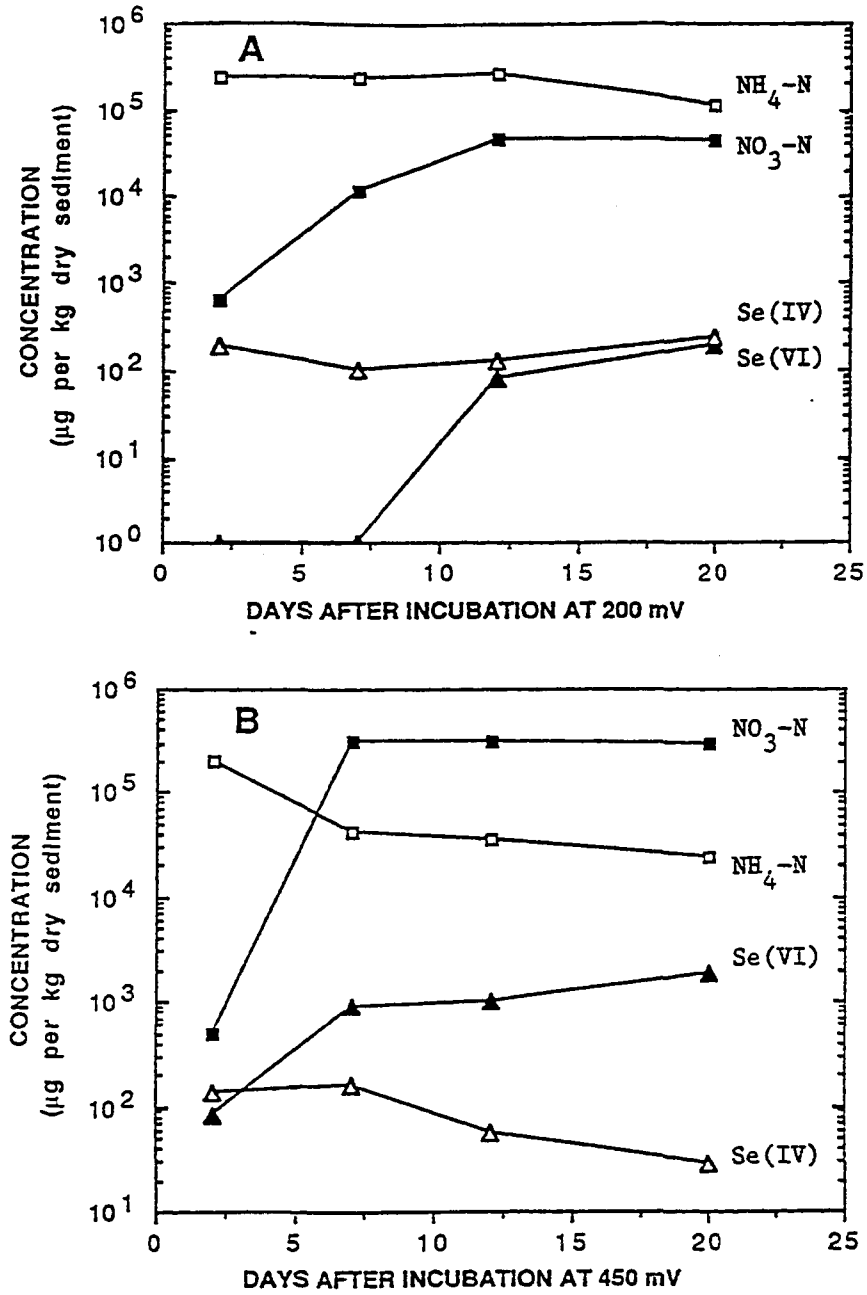


Figure 2: Ammonium/nitrate and selenite/selenate transformations during a 20-day incubation period. A) at 200 mV. B) at 450 mV.

sulfides leads to increases in soluble selenium species. The released Se(-II,0) is quickly oxidized to selenite. We also found that the oxidation of selenite to selenate occurred at a considerable higher Eh than the sulfide to sulfate oxidation. The oxidation rate of selenite to selenate is rather slow and is a function of the redox potential. Selenate was detected only when nitrate was present. From our experiments, it is difficult to calculate exact transformation rates because adsorption-desorption reactions occur simultaneously with the oxidation reactions.

It is clear that selenium solubility increases with increased redox potential. It also seems that the chemistry of selenium under reduced conditions is closely related to that of iron. Recently Elrashidi et al. (1987), using thermodynamic data to develop chemical equilibria reactions and constants of selenium in soils, also reported very low solubilities of selenides under reduced conditions. When an iron sulfide mineral forms in natural waters or sediments, the first phase to precipitate is usually an unstable monosulfide (Berner, 1970). Solubility products of iron monoselenide and sulfides are given in Table 3. If we assume that selenide can substitute for sulfide in a solid solution phase, for example, troilite (Fe(S,Se)) then from the following equilibrium reaction

$$FeS + Se^{2-} = FeSe + S^{2-} \qquad (4)$$

with $\log K = \log (a_{FeSe} / a_{FeS}) + \log (a_{S}2- / a_{Se}2-) = 9.79$, it can be seen that even in the presence of high sulfide concentrations only a very small amount of selenide is needed in order to get supersaturation with respect to the iron selenide component in the solid solution. Over time monosulfides are generally oxidized to pyrite ($FeS + S^0 = FeS_2$)

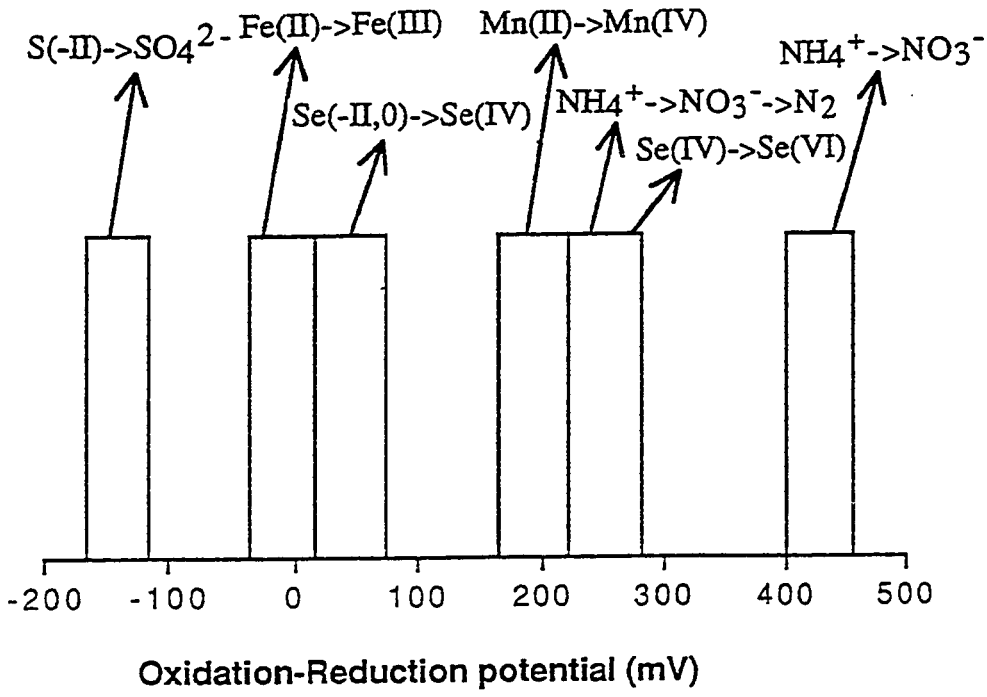


Figure 3: Sequential oxidation of several redox systems in Kesterson Reservoir sediments.

Table 3: Solubility products of selected iron sulfides and iron selenide at 25^0 C and 1 bar.

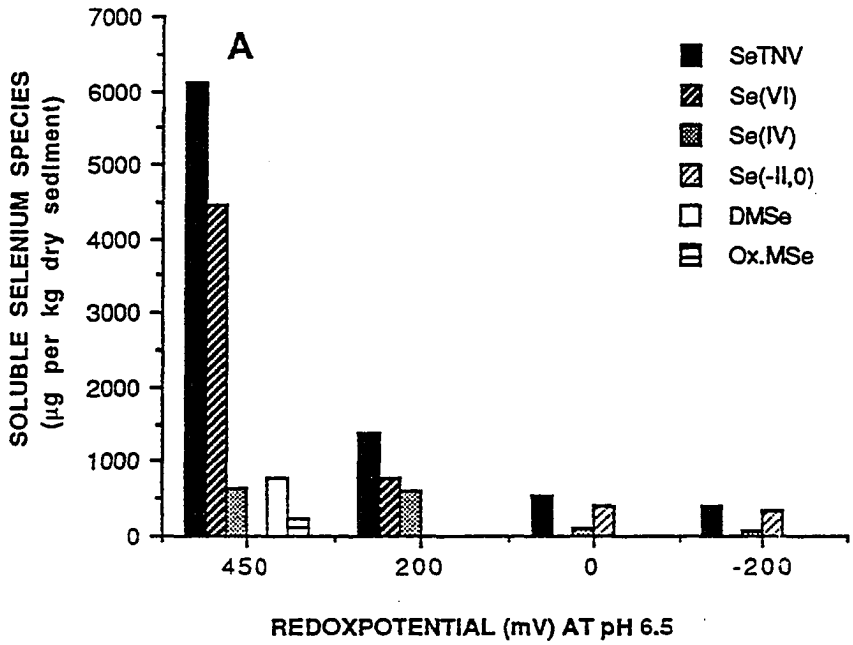
Mineral	Reaction products	-log(Ksp)	Ref.
α-$Fe_{0.95}S$(Pyrrhotite)	$0.85\ Fe^{2+} + 0.10\ Fe^{3+} + S^{2-}$	18.74	(Lindsay,1979)
α-FeS(Troilite)	$Fe^{2+} + S^{2-}$	16.21	(Lindsay,1979)
FeS_2(Pyrite)	$Fe^{2+} + S_2^{2-}$	26.93	(Lindsay,1979)
FeS_2(Markasite)	$Fe^{2+} + S_2^{2-}$	26.23	(Lindsay,1979)
FeSe(Achavalite)	$Fe^{2+} + Se^{2-}$	26.00	(Elrashidi et al.,1987)

(Berner, 1970), and it is very likely that in the presence of elemental sulfur the reaction FeSe + S^0 = FeSeS exists.

Influence of redox potential and pH on selenium solubility, speciation and volatilization

The redox-pH chemistry of indigenous selenium in Kesterson Reservoir sediments in relation to its solubility and its distribution among the various chemical species was determined (experiment two). Figure 4 shows the species distribution of total soluble selenium after 4 weeks of incubation at four different redox levels (-200, 0, 200, and 450 mV) ranging from strongly reduced to well oxidized. Four suspension pH levels (6.5, natural, 8.5, and 9) were selected and maintained during the incubation period. Incubations at pH values lower than 6.5 led to a massive dissolution of $CaCO_3$ and were therefore not included in this study. Total non volatile selenium (SeTNV) represents the sum of the inorganic (Se(-II,0), Se(IV), Se(VI)), and organic (DMSe and Ox.MSe) selenium compounds in solution at the time of sampling.

The selenium solubility strongly increased with increasing redox potential for all pH treatments. The pH had a major effect upon both the levels and chemical forms of dissolved selenium. In general, the selenium solubility was lowest in the incubations at natural pH. Both an increase or decrease in pH led to a higher amount of total soluble selenium. The highest total soluble selenium concentrations were found at a pH of 6.5. Up to 67 % of the total Se present in the sediment was found to be soluble at the high redox level (450 mV). This was due to the higher solubility of the iron sulfides and the concurrent release of selenium into solution. The precipitation of Ca^{2+} and SO_4^{2-} as gypsum,



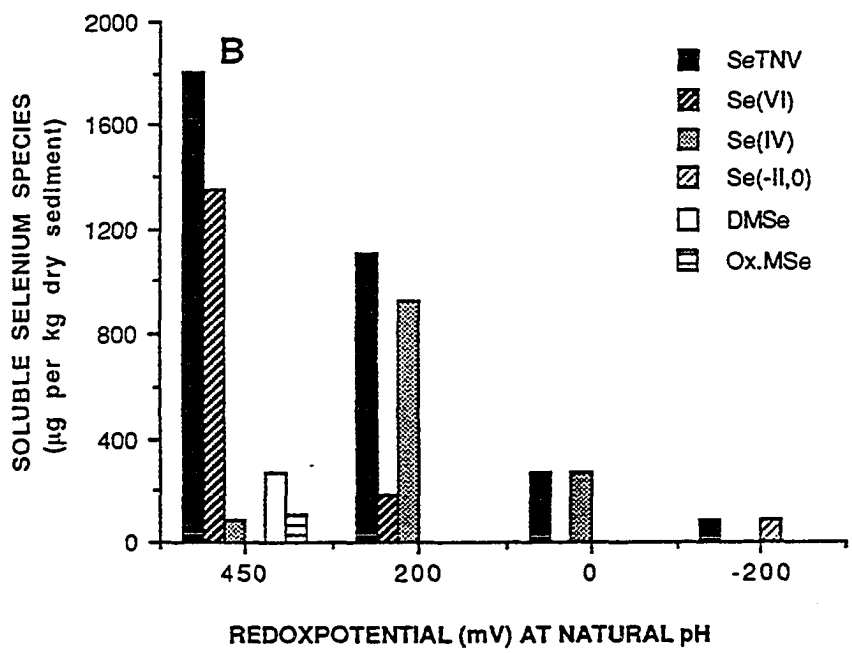


Figure 4: Distribution of soluble selenium species after a 28-day incubation period under controlled redox and pH conditions.
A) incubations at pH 6.5. B) incubations at natural pH (7.5 for 450 mV, 7.8 for 200 mV, 7.9 for 0 mV, and 8.1 for -200 mV).

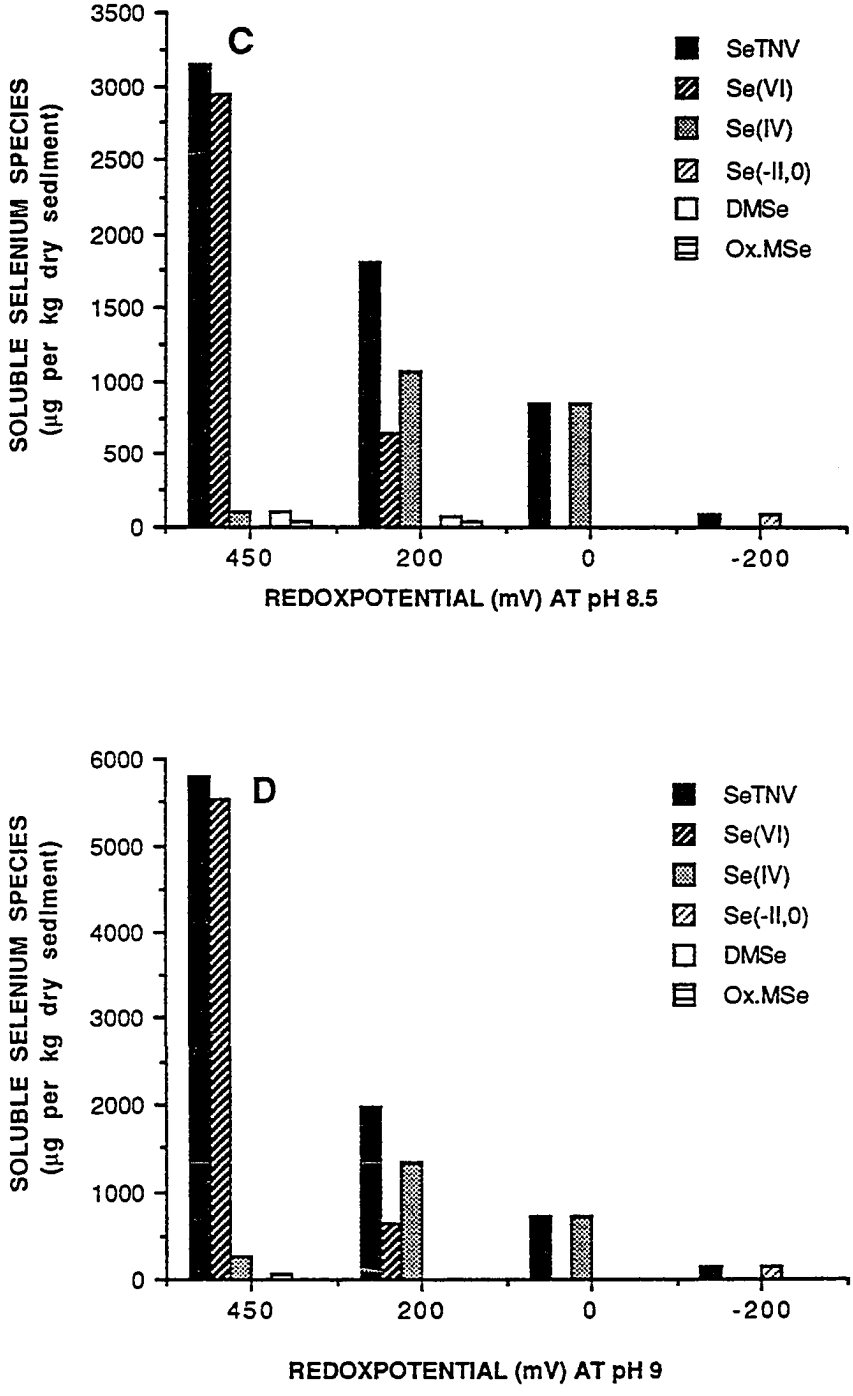


Figure 4: Distribution of soluble selenium species after a 28-day incubation period under controlled redox and pH conditions. C) incubations at pH 8.5. D) incubations at pH 9.

maintained the reactions in eq (2) and (3). Presser and Barnes (1984) reported a small substitution of SeO_4^{2-} for SO_4^{2-} in gypsum precipitated from water samples of the Kesterson Reservoir. In our experiment we did not find evidence of precipitation of a $CaSeO_4$ or $CaSeO_3$ phase, although the formation of such highly soluble compounds is probably possible in conditions of a dry and hot climate.

The increase in soluble selenium at pH values greater than 7.5 was significant only at 450 mV. Under the oxidized conditions (450 mV), 20 - 63 % of the total Se present in the sediment was solubilized, depending on the pH. This increase can be explained by the decrease in adsorptive capacity of the soil, especially from the oxidized iron forms for selenite with increasing pH. The adsorption processes of selenite and selenate have been extensively studied in recent years (Balistrieri and Chao, 1987; Bar-Yosef and Meek, 1987; Geering et al., 1968; Neal et al., 1987a, b). It is generally accepted that selenite adsorption decreases with increasing pH in the range 4 to 9 and that selenate adsorption is minimal under most pH conditions. The oxidation of iron sulfides resulted in the formation of hydroxylated ferric oxides whose surfaces can adsorb selenite and to a much lesser extent selenate.

The species distribution of selenium identified in the present study is consistent with the stability field of Se species in theoretically derived Eh-pH diagrams (Coleman, 1957; Howard, 1977; Neal et al., 1987a). Selenate was the major dissolved species under highly oxidized conditions, constituting 95% at higher pH's (8.5, 9) to 75% at lower pH's (7.5, 6.5) of the SeTNV. The Se(-II,0) concentrations were below the detection limit at the high redox levels and the Se(IV) only became detectable at the lower pH levels. At 200 mV, the major part of

the SeTNV (60-78%) was in the selenite form. When incubated at 0 mV there seems to be a rapid oxidation of the Se(-II,0) to selenite since no Se(-II,0) could be detected. No oxidation of selenite to selenate occurred at 0 mV during the 4 week incubation period. In the reduced (-200 mV) treatment, Se(-II,0) comprised 80-100% of the SeTNV. Selenite was detected only at pH 6.5.

Dissolved DMSe and oxidized methylated selenium compounds were detected only in the aerobic incubations. DMSe comprised 15% of the SeTNV, while the Ox.MSe fraction made up to 5% of the SeTNV. Assimilation of selenite and reductive methylation have been proposed as first steps in the methylation pathway of selenium (Challenger, 1945; Doran and Alexander, 1976). Cooke and Bruland (1987) showed outgassing of selenium in the biologically active Kesterson Reservoir to be substantial. They suggested that the production of DMSe occurred by intra- and / or extracellular transformation of biogenically derived Se-methylselenomethionine. Although we found dissolved methylated selenium compounds only under aerobic conditions, selenium volatilization under anaerobic conditions has also been reported (Challenger, 1945; Doran and Alexander, 1976; Reamer and Zoller, 1980). It is important to note that in these studies very high selenium concentrations were added to the soil. In the experiment reported here, solubility of indigenous selenim was very low under the reduced conditions (Tables 1 and 2). Contamination of the analytical grade-HNO_3 with selenium (up to 20 ng ml^{-1}), used to trap evolved selenium species, made it difficult to determine the exact amount of selenium volatilized. However, after making the appropriate corrections, we found selenium volatilization to

be significant only at 200 and 450 mV. No evidence was found for selenium volatilization under reduced conditions in our experiments.

CONCLUSIONS

Sediment redox potential and pH were shown to control the speciation and solubility of selenium. At low redox levels selenium solubility was low and controlled by an iron selenide phase. Total soluble selenium concentrations substantially increased upon oxidation or increase in sediment redox potential. Under highly oxidized conditions, selenate became the major species in solution and soluble selenium concentrations reached a maximum. Dimethyl selenide and other dissolved methylated selenium compounds were detected only under oxidized conditions. Redox potential and pH exhibit a major impact on selenium speciation, solubility, and volatilization and are therefore of paramount importance in the study of selenium biogeochemistry.

ACKNOWLEDGMENTS

We are grateful to the U.S. Geological Survey for collecting and providing the sediments used in this study.

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CHAPTER IV

BIOGEOCHEMICAL BEHAVIOR OF SELENIUM IN ANOXIC SOILS AND SEDIMENTS: AN EQUILIBRIUM THERMODYNAMICS APPROACH.

ABSTRACT

Equilibrium thermodynamic calculations were performed to evaluate mineral stability in anoxic soil and sediment porewater systems in which reducing conditions lead to microbially mediated transformations of Se oxyanions. pe-pH diagrams displaying mineral stability boundaries in the Fe-S-Se-H_2O system are presented. Several diagrams were constructed assuming typical concentrations of dissolved species for anaerobic soil and sediment porewaters. Under reducing conditions, elemental Se and the formation of FeSe or $FeSe_2$ control Se solubility. Native Se has a wide stability field, particularly under acid conditions. Under weakly acid to alkaline reducing conditions the formation of iron selenides is favored. If we assume that selenide can substitute for sulfide in a solid solution phase, precipitated FeS will contain an FeSe component. Because ironselenides are thermodynamically unstable with respect to their sulfur counterparts both FeS and FeS_2 are important in controlling the geochemical and environmental behavior of Se. Under conditions of FeS_2 formation, FeSe and $FeSe_2$ become unstable and elemental Se is produced.

INTRODUCTION

Bacterial mineralization of organic matter in flooded soils and anoxic sediments proceeds by reduction of electron acceptors and results in chemical changes within the interstitial waters. These changes include denitrification; manganese, iron, and sulfate reduction; and methane formation. Quantitatively iron and sulfate are the most important electron acceptors. One therefore commonly encounters high concentrations of dissolved iron and sulfides and the resultant formation of reduced iron minerals in anoxic soils and sediments (Berner, 1970; King et al., 1985). Less abundant elements may also serve as oxidizing agents, and recently it has been shown that selenium oxyanions can serve as electron acceptors for bacterial respiration (Mikkelsen et al., 1989; Oremland et al., 1989; Zehr et al., 1987).

The chemistry of selenium (Se) resembles that of sulfur (S) because of its proximity to it within group VI A. Se, like S, can exist in four different oxidation states: selenide (Se(-II)), elemental selenium (Se(0)), selenite (Se(IV)), and selenate (Se(VI)). Elevated Se concentrations in soils, sediments and natural waters have been associated with metal refining operations (Nriagu and Wong, 1983), and coal and petroleum by-products including coal fly ash wastes (Adriano et al., 1980). Recent discovery of toxic Se concentrations in soils and agricultural drainage waters in central California (Wiggett and Alfors, 1986) lead to a renewed interest in the environmental behavior of Se. For the pH and redox conditions in most aqueous environments, selenium exists as an oxyanion in the selenate (SeO_4^{2-}), selenite (SeO_3^{2-}), or biselenite ($HSeO_3^-$) form (Coleman and Delevaux, 1957; Neal et al., 1987). Selenium oxyanions are reported to be extremely toxic to plants

(Mayland et al., 1989; Mikkelsen et al., 1989), animals (Ohlendorf, 1989) and humans (Rosenfeld and Beath, 1974). It is well accepted that adsorption-desorption reactions control the geochemical behavior of Se oxyanions under oxidized conditions (Balistrieri and Chao, 1990; Neal et al., 1987). Based upon equilibria thermodynamic calculations, Elrashidi et al. (1987) concluded that metal-selenite and in particular metal-selenate minerals are too soluble to persist in soils. Although selenium oxyanions are reported to be stable with respect to changing redox conditions in an inorganic system, the presence of organic matter and the accompanying bacteria almost guarantees their reduction. Elemental or native selenium is thought to be rare, although it has been reported in some sediments (Oremland et al., 1989) and is occasionaly mixed with native sulfur (Wiggett and Alfors, 1986). It has also been noted that Se^{2-} can ionically substitute for sulfur in metallic sulfide minerals. Especially important are chalcopyrite ($CuFeS_2$), and pyrite (FeS_2) (Wiggett and Alfors, 1986), although Se may also subsitute in other sulfides, such as galena (PbS) and pyrrhotite (FeS) (Bethke and Barton, 1971; Simpson, 1960; Tishendorf and Ungethum, 1964). A few selenides occur as minerals: clausthalite (PbSe), achavalite (FeSe), and ferroselite ($FeSe_2$) (Coleman, 1959; Sindeeva, 1964).

In view of the above described geochemical considerations, it would appear that the formation of non-toxic elemental Se and/or insoluble ironselenides in flooded soils and anoxic sediments could act as an environmentally important sink for selenium. To better understand the processes involved in selenium removal, mineral stability in the system Fe-S-Se-H_2O was theoretically evaluated. Although most of the reactions are microbially mediated they will eventually approach equilibrium

conditions, which makes a thermodynamic approach possible. Based on equilibrium thermodynamic calculations, pe-pH stability diagrams were constructed and, qualitative predictions were made concerning the fate of Se under anoxic conditions.

THERMODYNAMIC CONSIDERATIONS

Equilibrium reactions for dissolved species and solid phases in the system Fe-S-Se-H_2O were written. The equilibrium constants were calculated from selected standard free energies of formation, tabulated for 25°C and 1 bar total pressure (Wagman et al., 1982). The Gibbs free energy of formation for $FeSe_2$ was taken to be -96.97 kJ/mole (Howard, 1977). The calculated solubility product for FeSe (10^{-22}) is considerably greater than earlier reported values (10^{-26}) (Smith and Martell, 1976). Once the equilibrium constant K was determined, the appropriate phase boundary was calculated, expressed in terms of pe and pH, and plotted on a pe-pH diagram. Redox reactions, as well as calculated phase boundaries are listed in Tables 1, 2, and 4. The expression 59.2 x pe = Eh (mV) can be used to relate calculated pe values with experimentally measured redox potentials.

Although not shown in this manuscript, the mineral stability relations were also evaluated for temperature and pressure conditions other than the standard state conditions of temperature (25° C) and pressure (1 bar) using standard enthalpy (Smith and Martell, 1976; Wagman et al., 1982) and molar volume (Millero, 1971; Robie et al., 1978) data. Although the positions of the fields shifted somewhat to lower pH values (with increasing temperature) or higher redox levels (with increasing pressure), the shapes and the sizes of the stability

fields were maintained. The latter calculations illustrated that redox-pH stability diagrams calculated using standard free energy data, do not significantly change for temperature and pressure ranges normally encountered in soils and sediments. Both redox and pH remained the dominant environmental parameters determining mineral stability in the Fe-S-Se-H_2O system.

RESULTS AND DISCUSSION

Mineral stability in the FeS-FeSe-H_2O system

Redox reactions in table 1 were used to construct a pe-pH diagram showing the predominance areas for Se species at 25°C and 1 bar total pressure (Fig.1). Calculations were made for a total Se activity of 10^{-6} ($a_{Setot} = 10^{-6}$). To construct the boundary lines eq.(1)-(15) were used, a_{H2O} was assumed to be 1, and the activities of species in equilibrium were made equal. As can be seen, the main components of the system are H_2Se, HSe^-, Se^o, H_2SeO_3, $HSeO_3^-$, SeO_3^{2-}, $HSeO_4^-$, and SeO_4^{2-}. Similar redox-pH diagrams were recently drawn and used to discuss the equilibrium distribution of dissolved Se species in aqueous solutions under earth surface conditions (Mayland et al., 1989; Neal et al., 1987).

However, a more useful diagram than those containing only the predominance areas of dissolved Se species is a phase diagram containing equilibria reactions involving both dissolved ions and solid phases. In order to evaluate mineral stability in the FeS-FeSe-H_2O system contour lines for equal activities of the Se^{2-} ion were calculated. The following example illustrates the calculation of these contour lines: the $a_{Se2-} = 10^{-15}$ contour line intersects the predominance areas of

Table 1: Equilibrium reactions, log K values, and phase diagram boundaries for the Fe - Se - H_2O system at 25° C and 1 bar of total presssure.

Reaction	Log K	phase diagram boundary
(1) $H_2Se = HSe^- + H^+$	-3.82	$pH = 3.82 + \log (aHSe^-/aH_2Se)$
(2) $HSe^- = Se^{2-} + H^+$	-14.9	$pH = 14.9 + \log (aSe^{2-}/aHSe^-)$
(3) $H_2SeO_3 = HSeO_3^- + H^+$	-2.57	$pH = 2.57 + \log (aHSeO_3^-/aH_2SeO_3)$
(4) $HSeO_3^- = SeO_3^{2-} + H^+$	-7.30	$pH = 7.30 + \log (a\ SeO_3^{2-}/aHSeO_3^-)$
(5) $H_2SeO_3 = SeO_3^{2-} + 2H^+$	-9.88	$pH = 4.94 + 1/2\log (a\ SeO_3^{2-}/aH_2SeO_3)$
(6) $HSeO_4^- = SeO_4^{2-} + H^+$	-1.90	$pH = 1.90 + \log (a\ SeO_4^{2-}/aHSeO_4^-)$
(7) $Se^o + H^+ + 2e^- = HSe^-$	-7.71	$pe = -3.85 - 1/2\log aHSe^- - 1/2pH$
(8) $Se^o + 2H^+ + 2e^- = H_2Se$	-3.89	$pe = -1.94 - 1/2\log aH_2Se - pH$
(9) $SeO_3^{2-} + 6H^+ + 4\ e^- = Se^o + 3H_2O$	59.8	$pe = 14.96 - 1/4\log (a\ Se^o/a\ SeO_3^{2-}) - 3/2pH$
(10) $HSeO_3^- + 5H^+ + 4e^- = Se^o + 3H_2O$	52.5	$pe = 13.13 - 1/4\log (a\ Se^o/aHSeO_3^-) - 5/4pH$
(11) $H_2SeO_3 + 4H^+ + 4e^- = Se^o + 3H_2O$	50.0	$pe = 12.50 - 1/4\log (a\ Se^o/aH_2SeO_3) - pH$
(12) $HSeO_4^- + 3H^+ + 2e^- = H_2SeO_3 + H_2O$	37.0	$pe = 18.49 - 1/2\log(aH_2SeO_3/aHSeO_4^-) - 3/2pH$
(13) $SeO_4^{2-} + 4H^+ + 2e^- = H_2SeO_3 + H_2O$	38.9	$pe = 19.44 - 1/2\log(aH_2SeO_3/a\ SeO_4^{2-}) - 2pH$
(14) $SeO_4^{2-} + 3H^+ + 2e^- = HSeO_3^- + H_2O$	36.3	$pe = 18.16 - 1/2\log(aHSeO_3^-/a\ SeO_4^{2-}) - 3/2pH$
(15) $SeO_4^{2-} + 2H^+ + 2e^- = SeO_3^{2-} + H_2O$	29.0	$pe = 14.50 - 1/2\log(a\ SeO_3^{2-}/a\ SeO_4^{2-}) - pH$
(16) $H_2Se = Se^{2-} + 2H^+$	-18.7	$pH = 9.38 + 1/2\log (aSe^{2-}/aH_2Se)$
(17) $Se^o + 2e^- = Se^{2-}$	-22.6	$pe = -11.3 - 1/2\log aSe^{2-}$
(18) $SeO_3^{2-} + 6H^+ + 6\ e^- = Se^{2-} + 3H_2O$	37.2	$pe = 6.19 - 1/6\log (aSe^{2-}/a\ SeO_3^{2-}) - pH$
(19) $HSeO_3^- + 5H^+ + 6e^- = Se^{2-} + 3H_2O$	29.9	$pe = 4.98 - 1/6\log (aSe^{2-}/aHSeO_3^-) - 5/6pH$
(20) $H_2SeO_3 + 4H^+ + 6e^- = Se^{2-} + 3H_2O$	27.1	$pe = 4.5 - 1/6\log (aSe^{2-}/aH_2SeO_3) - 2/3pH$
(21) $SeO_4^{2-} + 8H^+ + 8e^- = Se^{2-} + 4H_2O$	66.2	$pe = 8.27 - 1/8\log(aSe^{2-}/a\ SeO_4^{2-}) - pH$
(22) $HSeO_4^- + 7H^+ + 8e^- = Se^{2-} + 4H_2O$	64.3	$pe = 8.03 - 1/8\log(aSe^{2-}/aHSeO_4^-) - 7/8pH$
(23) $Fe^{2+} + Se^{2-} = FeSe$	-22.0	
(24) $Fe^{3+} + e^- = Fe^{2+}$	13.0	$pe = 13.0$
(25) $Fe(OH)_3 + 3H^+ = Fe^{3+} + 3H_2O$	3.57	$pH = 2.52$
(26) $Fe(OH)_3 + e^- + 3H^+ = Fe^{2+} + 3H_2O$	16.4	$pe = 20.43 - 3pH$
(27) $Fe(OH)_3 + Se(0) + 3e^- + 3H^+ = FeSe + 3H_2O$	15.8	$pe = 6.26 - pH$

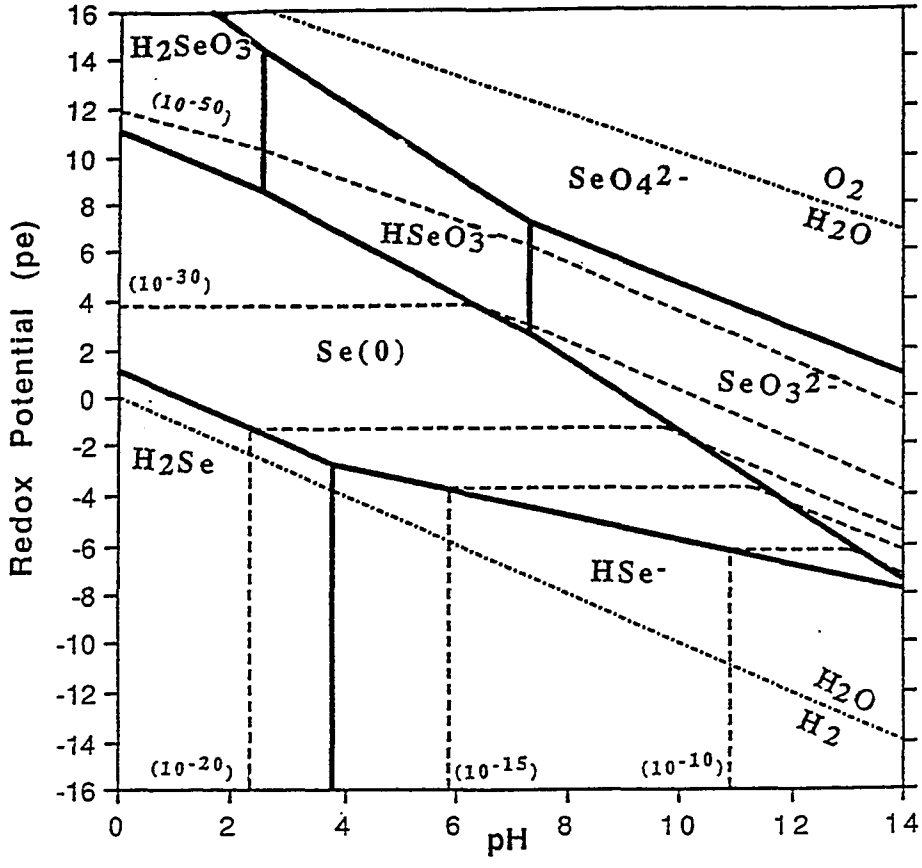

Figure 1: Predominance areas for dissolved selenium species calculated for a temperature of 25° C and 1 bar total pressure. Boundaries are drawn for $a_{Setot} = 10^{-6}$. Dashed lines represent contours of equal selenide activities.

HSe^-, Se^o, and SeO_3^{2-} and was calculated using the equations (2),(17), and (18). For $a_{Setot} = 10^{-6}$ and $a_{Se2-} = 10^{-15}$, eq.(2) becomes: $pH = 14.9 + \log(10^{-15}/10^{-6}) = 5.9$. The a_{Se2-} in this area is independent of pe and plots as a straight vertical line. In the native Se field, eq. (17) becomes $pe = -11.3 - 1/2\log 10^{-15} = -3.8$. This represents a straight line parallel to the X-axis. Substituting $a_{SeO3}^{2-} = 10^{-6}$ and $a_{Se2-} = 10^{-15}$ in eq.(18) describes the Se^{2-} contour line in the SeO_3^{2-} field: $pe = 6.19 - 1/6\log(10^{-15}/10^{-6}) - pH = 7.69 - pH$. Contour lines for other a_{Se2-} values were calculated in an analogous manner. When an aqueous solution reaches saturation equilibrium with respect to a mineral phase precipitation of that mineral phase will occur. Considering $a_{Fe2+} = 10^{-4}$, and the solubility product of FeSe = 10^{-22}, FeSe will start to precipitate when the a_{Se2-} reaches 10^{-18}. Using the data in Table 2, a graph similar to Figure 1 can be made for the sulfur species. pe-pH phase diagrams for the S species can be found throughout the literature (Drever, 1988; Garrels and Naesser, 1958) and contour lines for equal a_{S2-} are easily calculated using eq.(2), (11)-(14). In contrast to Se (Fig.1), the field of S^o is very small and only becomes important at $a_{Stot} > 10^{-1}$ or low solution pH (Garrels and Naesser, 1958). With a solubility product of 10^{-19} and assuming $a_{Fe2+} = 10^{-4}$, the formation of FeS will start at $a_{S2-} >$ or $= 10^{-15}$.

As was illustrated by Garrels (1960), several individually prepared pe-pH diagrams can be superimposed and the areas of mineral stability in the total system delineated. Calculated phase diagrams for the systems $Fe-Se-H_2O$ and $Fe-S-H_2O$ were overlaid and displayed as a composite diagram (Fig.2A, B). The predominance areas for dissolved Se and S

Table 2: Equilibrium reactions, log K values, and phase diagram boundaries for the S - H_2O system at 25° C and 1 bar of total presssure.

Reaction	Log K	phase diagram boundary
(1) $H_2S = HS^- + H^+$	6.99	$pH = 6.99 - \log (aHS^-/aH_2S)$
(2) $HS^- = S^{2-} + H^+$	-12.9	$pH = 12.9 + \log (aS^{2-}/aHS^-)$
(3) $HSO_4^- = SO_4^{2-} + H^+$	-1.99	$pH = 1.99 + \log (a\ SO_4^{2-}/aHSO_4^-)$
(4) $S^o + H^+ + 2e^- = HS^-$	2.11	$pe = 1.05\text{-}1/2\log\ aHS^- - 1/2pH$
(5) $S^o + 2H^+ + 2e^- = H_2S$	4.87	$pe = 2.43 - 1/2\log\ aH_2S - pH$
(6) $HSO_4^- + 9H^+ + 8e^- = H_2S + 4H_2O$	38.6	$pe = 4.82\ \text{-}1/8\log(aH_2S/a\ HSO_4^-) - 2pH$
(7) $HSO_4^- + 7H^+ + 6e^- = S + 4H_2O$	33.7	$pe = 5.62\ \text{-}1/6\log(1/aHSO_4^-) - 7/6pH$
(8) $SO_4^{2-} + 10H^+ + 8e^- = H_2S + 4H_2O$	40.6	$pe = 5.07\ \text{-}1/8\log(aH_2S/a\ SO_4^{2-}) - 10/8pH$
(9) $SO_4^{2-} + 9H^+ + 8e^- = HS^- + 4H_2O$	33.6	$pe = 4.20\ \text{-}1/2\log(a\ HS^-/a\ SO_4^{2-}) - 9/8pH$
(10) $SO_4^{2-} + 8H^+ + 8e^- = S + 4H_2O$	35.7	$pe = 5.95 - 1/6\log(1/aSO_4^{2-}) - 4/3pH$
(11) $H_2S = S^{2-} + 2H^+$	-19.9	$pH = 9.95 + 1/2\log (aS^{2-}/aH_2S)$
(12) $S^o + 2e^- = S^{2-}$	-15.0	$pe = -7.51\ \text{-}1/2\log\ aS^{2-}$
(13) $HSO_4^- + 7H^+ + 8e^- = S^{2-} + 4H_2O$	18.7	$pe = 2.33\text{-}1/8\log(aS^{2-}/a\ SO_4^{2-}) - 7/8pH$
(14) $SO_4^{2-} + 8H^+ + 8e^- = S^{2-} + 4H_2O$	20.7	$pe = 2.55\ \text{-}1/8\log(aS^{2-}/a\ SO_4^{2-}) - pH$
(15) $Fe^{2+} + S^{2-} = FeS$	-19.0	

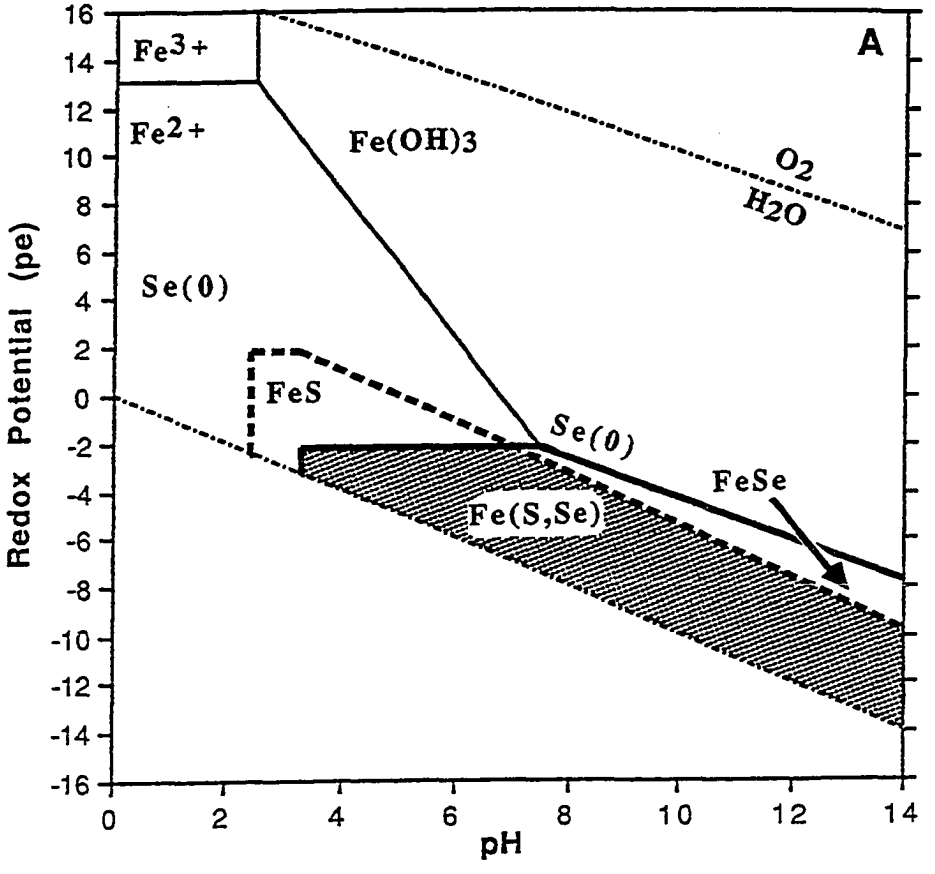

Figure 2A: pe-pH diagram for the system Fe-Se-S-H_2O at 25° C and 1 bar total pressure. Solid solution boundaries are drawn for $a_{Setot} = 10^{-6}$, $a_{Stot} = 10^{-2}$, $a_{Fe2+} = 10^{-4}$. The heavier solid lines indicate the FeSe stability field. The heavier dashed lines indicate the FeS stability field. The shaded area represent the area of Fe(S,Se) solid solution.

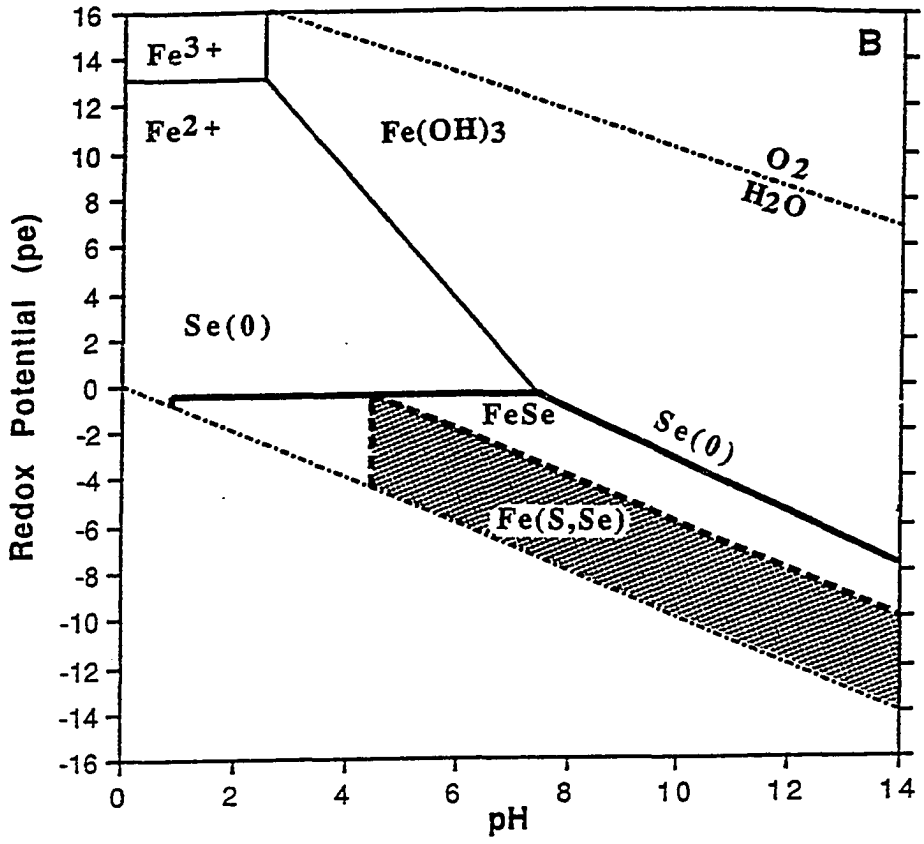

Figure 2B: pe-pH diagram for the system Fe-Se-S-H_2O at 25° C and 1 bar total pressure. Solid solution boundaries are drawn for $a_{Setot} = 10^{-4}$, $a_{Stot} = 10^{-4}$, $a_{Fe2+} = 10^{-4}$. The heavier solid lines indicate the FeSe stability field. The heavier dashed lines indicate the FeS stability field. The shaded area represent the area of Fe(S,Se) solid solution.

were omitted for clarity, and $Fe(OH)_3$ was assumed to control Fe solubility under oxidized conditions. Since pe-pH diagrams are constructed under conditions of constant activities of ions several phase diagrams can be made. Redox reactions provided in the tables allow for the calculation of the stability relations for any specified set of ion activities. Figures 2A and 2B, represent stability relations in the Fe-Se-S-H_2O system under conditions of $a_{Fe2+}=10^{-4}$, $a_{Se2-}=10^{-6}$, $a_{S2-}=10^{-2}$ and $a_{Fe2+}=10^{-4}$, $a_{Se2-}=10^{-4}$, $a_{S2-}=10^{-4}$; respectively.

It is interesting to note that, due to the small value of their solubility product, both FeSe and FeS start to precipitate well outside the predominance area of Se^{2-} and S^{2-}, respectively. As soon as dissolved Fe and Se^{2-} are simultaneously present FeSe will be formed. Under the conditions specified in Fig. 2A, FeSe is stable only at neutral to alkaline pH. Se^{o} has a wide stability field, particularly under acid conditions, and overlaps most of the FeSe stability field. The crystalline form of elemental Se is monoclinic and is referred to as red crystalline Se. The two amorphous forms of elemental Se are the red amorphous, and glassy black varieties (Sindeeva, 1964). Ironselenides are formed at redox levels higher than those required for the formation of iron sulfides. Under these conditions no FeS will be formed and the FeSe will be S free. Precipitation of FeS starts when a_{S2-} reaches 10^{-15} and the precipitated FeS will be Se-bearing.

The occurrence of the described mineral assemblage fits into the picture of mineral formation in anaerobic soil and sediment porewaters. In flooded soils, anoxic brackish and fresh water sediments initial sulfur concentrations are normally low and sulfate is quickly reduced. The produced H_2S reacts with Fe to form highly insoluble FeS minerals

(Berner, 1980). If present, dissimilatory reduction will also remove soluble selenium oxyanions (Mikkelsen et al., 1989; Oremland et al., 1989; Zehr and Oremland, 1987). As can be seen from Fig. 2, upon reduction Se^{o} will limit selenium solubility over a wide pH range. However, under weakly acid to alkaline conditions both Se^{o} and FeSe are thermodynamically stable. Although the stability field of FeSe is relatively small, it is geochemically important because it coincides with redox-pH conditions commonly encountered in anaerobic soil or sediment porewaters (Becking et al., 1960). Strongly reducing conditions will favor the formation of Se-bearing FeS. The formation of an Fe(S,Se) solid solution may be another important phase in the environmental cycling of Se.

Once all S and Se are depleted and precipitated, the concentration of dissolved Fe could build up by continued bacterial reduction until supersaturation will be reached with respect to some iron mineral. A typical mineral formed under these conditions is siderite ($FeCO_3$) (Becking et al., 1960; Garrels, 1960). $FeCO_3$ has a very limited stability field, and should only be considered if dissolved carbonate activity is very high ($a_{CO32-} > 10^{-1}$) and reduced S very low ($a_{Stot} < 10^{-5}$) (Garrels, 1960; Nordstrom and Munoz, 1985). In contrast to most anoxic sediments, some flooded soils are characterized by the presence of high carbonate and low sulfide activities. The formation of siderite in these soils will decrease the size of the FeSe stability field and will result in the production of elemental Se.

Fe(S,Se) solid solutions

Selenides have been reported to form extensive solid solutions with sulfides (Bethke and Barton, 1971; Simpson, 1960) over a wide temperature range. The rapid rates of the solid state reactions implies that solid solutions should be considered even in low temperature environments. Recently, we found that the oxidation and chemical weathering of iron sulfides in a selenium contaminated sediment lead to increases in soluble Se species (Masscheleyn et al., 1990). If we assume that Se^{2-} can substitute for sulfide in a solid solution phase, for example, pyrrhotite, then from the equilibrium reaction: FeS + Se^{2-} = FeSe + S^{2-}, the mole fraction of both components (X_{FeSe} and X_{FeS}) in the Fe(S,Se) solid solution can be calculated using the following two equations:

(1) $X_{FeSe} + X_{FeS} = 1$

(2) $X_{FeSe}/X_{FeS} = (10^{-19}/10^{-22}) \times (a_{Se2-}/a_{S2-})$.

Except under acid conditions, all of the precipitated FeS will contain an FeSe component in solid solution (Fig.2). The variation of the (a_{Se2-}/a_{S2-}) ratio within the Fe(S,Se) stability field was calculated for specified values of pe and pH. Within the Fe(S,Se) field both activities increase as pH increases, that of S^{2-} faster than that of Se^{2-}. Table 3 illustrates the variation of (a_{Se2-}/a_{S2-}) below $a_{S2-} = 10^{-15}$ for the conditions specified in Figure 2B. Sulfide activities were calculated using eq.(2), Table 2. Unless otherwise indicated, selenide acitivities were computed using eq.(2), Table 1. The X_{FeSe} in the Fe(S,Se) solid solution varied from 0.90 up to 0.99 under weakly acid conditions. For the conditions specified in figure 2A, the X_{FeSe} in the solid solution

Table 3: Variation of (a_{Se2-}/a_{S2-}) within the Fe(S,Se) stability field and the mole fraction of the FeSe component in solid solution. Calulations were done assuming $a_{Fe2+} = a_{Setot} = a_{Stot} = 10^{-4}$.

pH	pe	log a_{Se2-}	log a_{S2-}	a_{Se2-}/a_{S2-}	X_{FeSe} in Fe(S,Se)
10	-6	-8.9	-6.9	10^{-2}	0.90
	-7	-8.9	-6.9	10^{-2}	0.90
	-8	-8.9	-6.9	10^{-2}	0.90
	-9	-8.9	-6.9	10^{-2}	0.90
	-10	-8.9	-6.9	10^{-2}	0.90
8	-5	-10.9	-8.9	10^{-2}	0.90
	-6	-10.9	-8.9	10^{-2}	0.90
	-7	-10.9	-8.9	10^{-2}	0.90
	-8	-10.9	-8.9	10^{-2}	0.90
6	-3	-16.6[a]	-11.9	10^{-5}	0.01
	-4	-14.6[a]	-11.9	10^{-3}	0.50
	-5	-12.9	-11.9	10^{-1}	0.99
	-6	-12.9	-11.9	10^{-1}	0.99

a: calculated using eq.(17), Table I

is generally less than 0.01. At pH < 5, FeSe becomes the dominant component in the Fe(Se,S) phase.

Mineral stability in the FeS_2-$FeSe_2$-H_2O system

In anaerobic saline environments or in sediments high in organic matter there is usually sufficient dissolved sulfate to react with all reduced Fe. In the presence of high sulfide concentrations the initially formed monosulfides are generally oxidized to pyrite (FeS_2). Enough H_2S is present to convert all of the FeS minerals into FeS_2 (Berner, 1970; Lord and Church, 1983). Although little information is available about mineral formation in a system containing Se and Fe, it is very likely that similar reactions result in the precipitation of $FeSe_2$. The stability of the mineral assemblages that could occur in a system containing Fe together with large initial S concentrations and Se were thermodynamically evaluated. The stability field for $FeSe_2$ (Fig.3) was delineated using an approach similar to the one used by Nordstrom and Munoz (1985) for the determination of FeS_2 stability. Equations (4) and (6), Table 4 were added in order to construct the left hand side stability boundaries. Fe_2O_3, rather than $Fe(OH)_3$, was assumed to control iron solubility under oxidizing conditions. For the ion activities specified in Fig. 3 elemental selenium will be thermodynamically preferred under both acid and alkaline conditions, at redox levels greater than pe = -0.41. Under more reduced conditions ferroselite becomes thermodynamically stable.

Figure 4 graphically displays the stability fields for elemental Se, and the ferroselite, pyrite and hematite minerals in the system Fe-Se-S-H_2O at 25°C and 1 bar total pressure. All equilibrium reactions and

Table 4: Equilibrium reactions, logK, and phase diagram boundaries for the system Fe-S-Se-H_2O. Calculated for 25° C and 1bar of total pressure and assuming $a_{Fe2+} = 10^{-4}$, $a_{Stot} = 10^{-1}$and, $a_{Setot} = 10^{-6}$.

	Reaction	Log K	Phase diagram boundary
(1)	$Fe^{2+} + 2HSeO_4^- + 14H^+ + 14e^- = FeSe_2 + 8H_2O$	177	pe = 11.6 - pH
(2)	$Fe^{2+} + 2SeO_4^{2-} + 16H^+ + 14e^- = FeSe_2 + 8H_2O$	181	pe = 11.8 - 8/7pH
(3)	$Fe_2O_3 + 4SeO_4^{2-} + 38H^+ + 38e^- = 2FeSe_2 + 19H_2O$	384	pe = 12.0 - 38/30pH
(4)	$Fe^{2+} + 2H_2Se = FeSe_2 + 4H^+ + 2e^-$	10.9	pe = 2.52 - 2pH
(5)	$FeSe + HSe^- = FeSe_2 + H^+ + 2e^-$	11.4	pe = -2.71 - 1/2pH
(6)	$FeSe_2 = Fe^{2+} + 2Se^0 + 2e^-$	-3.16	pe = -0.41
(7)	$Fe^{2+} + 2HSO_4^- + 14H^+ + 14e^- = FeS_2 + 8H_2O$	82.9	pe = 5.35 - pH
(8)	$Fe^{2+} + 2SO_4^{2-} + 16H^+ + 14e^- = FeS_2 + 8H_2O$	87.3	pe = 5.45 - 8/7pH
(9)	$Fe_2O_3 + 4SO_4^{2-} + 38H^+ + 38e^- = 2FeS_2 + 19H_2O$	196	pe = 6.40 - 38/30pH
(10)	$Fe^{2+} + 2H_2S = FeS_2 + 4H^+ + 2e^-$	5.67	pe = 0.16 - 2pH
(11)	$FeS + HS^- = FeS_2 + H^+ + 2e^-$	13.6	pe = -6.30 - 1/2pH
(12)	$FeS_2 = Fe^{2+} + 2S^0 + 2e^-$	-15.4	pe = 5.70
(13)	$Fe^{3+} + e^- = Fe^{2+}$	13.0	pe = 13.0
(14)	$Fe_2O_3 + 6H^+ = 2Fe^{3+} + 3H_2O$	-3.74	pH = 0.71
(15)	$Fe_2O_3 + 6H^+ + 2e^- = 2Fe^{2+} + 3H_2O$	22.2	pe = 15.1 - 3pH
(16)	$FeS_2 + HSe^- + 3H^+ + 2e^- = FeSe + 2H_2S$	-1.47	pe = -0.26 - 3/2pH
(17)	$FeS_2 + HSe^- + H^+ + 2e^- = FeSe + 2HS^-$	-12.5	pe = -7.25 - pH
(18)	$FeS_2 + 2Se^0 = FeSe_2 + 2S^0$	-12.2	

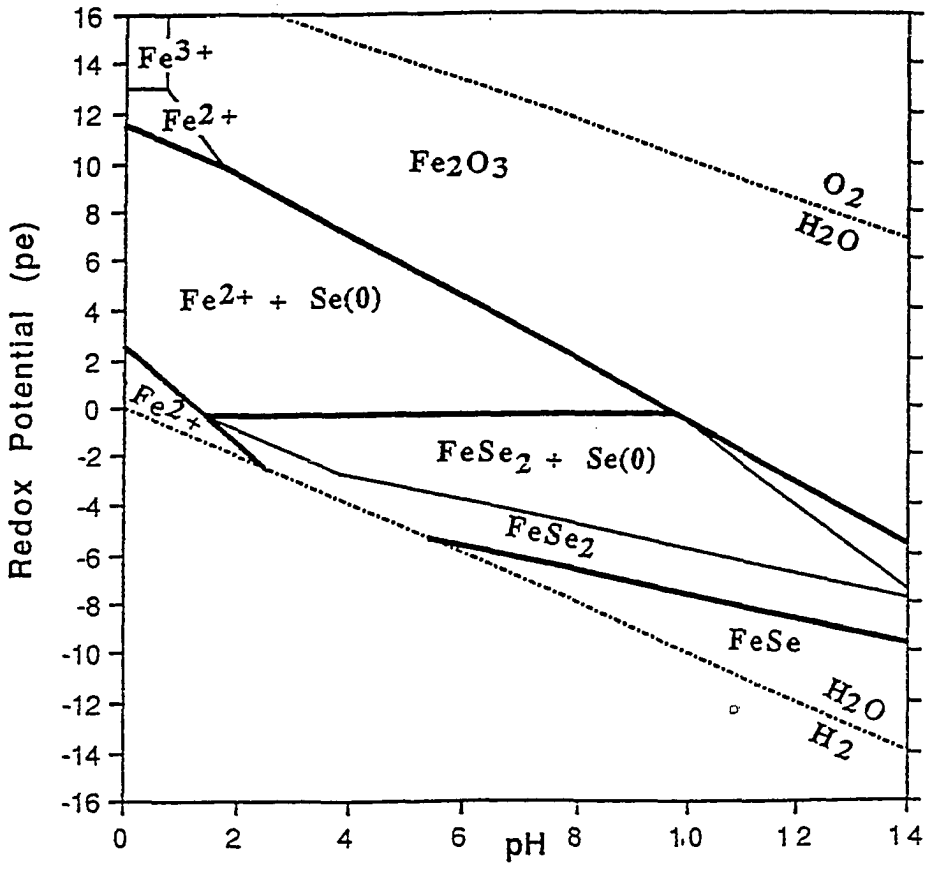

Figure 3: Stability of Fe_2O_3 and $FeSe_2$ at 25° C and 1 bar total pressure; assuming $a_{Setot} = 10^{-6}$ and $a_{Fe2+} = 10^{-4}$. The lighter solid lines within the $FeSe_2$ field represent the stability field for elemental Se.

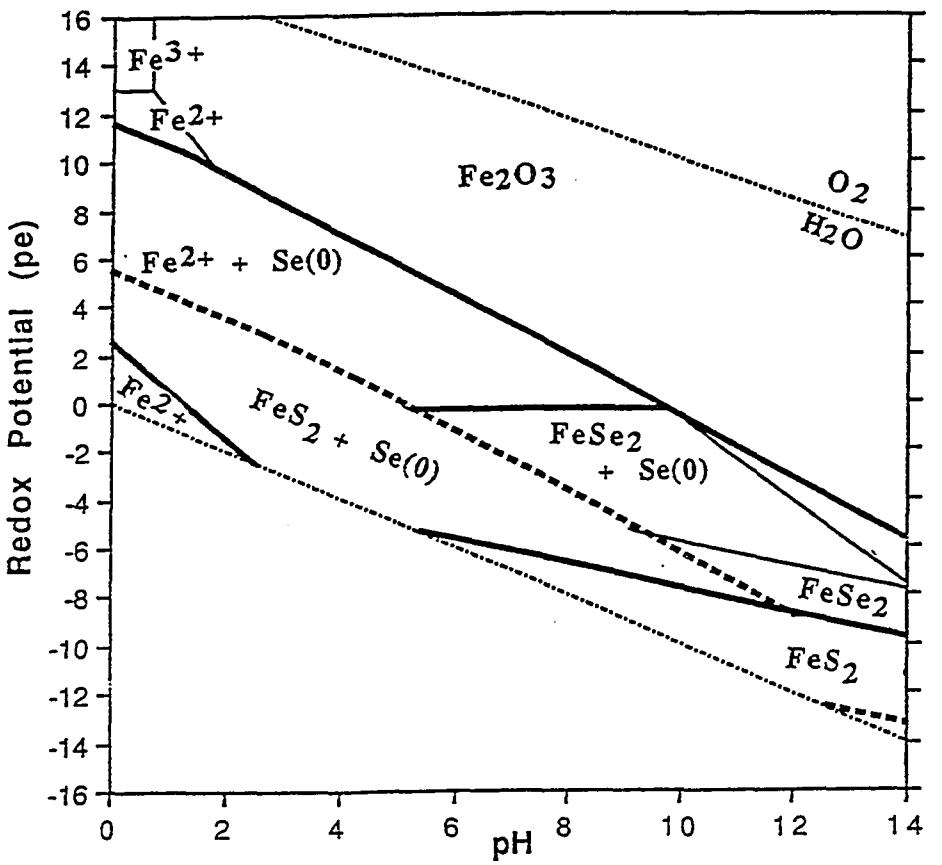

Figure 4: Stability of Fe_2O_3, FeS_2, and $FeSe_2$ at 25° C and 1 bar total pressure; assuming $a_{Setot} = 10^{-6}$, $a_{Stot} = 10^{-1}$, and $a_{Fe2+} = 10^{-4}$. The lighter solid lines within the $FeSe_2$ field represent the stability field for elemental Se. The heavier dashed lines indicate the FeS_2 stability field.

calculated phase boundaries used to construct this composite diagram are listed in Table 4. Although these reactions are not unique in representing equilibrium conditions in the Fe-S-Se-H_2O system, all of them are valid and, therefore, may be thermodynamically evaluated. The stability boundaries for reaction (16) and (17) plot below the lower stability line for water and were therefore not drawn. The diagram, constructed assuming values of $a_{Se2-} = 10^{-6}$, $a_{S2-} = 10^{-1}$ and $a_{Fe2+} = 10^{-4}$, shows some interesting relations. Ferroselite is stable in an environment more oxidizing than pyrite. In the presence of excess sulfur, both achavalite and ferroselite are thermodynamically unstable with respect to pyrite (eq.(16-18), Table 4). The selenium released in eq.(18) will be present as Se^o or can be incorporated in pyrite. Solid solution between pyrite and ferroselite is minimal, even at high temperatures and pressures, because pyrite is cubic and ferroselite is orthorhombic (Coleman, 1959). Coleman and Delevaux (1957) reported up to 4% of $FeSe_2$ in the pyrite structure. In contrast, up to 63% $FeSe_2$ was found in marcasite, the orthorhombic dimorph of pyrite.

Environmental implications

The interpretation of the equilibrium thermodynamic calculations and constructed pe-pH diagrams has implications for understanding and predicting the environmental behavior of Se in soils and sediments. For the pH and redox conditions in most soils and aerobic sediments, selenium would exist as an oxyanion in the selenate (SeO_4^{2-}), selenite (SeO_3^{2-}), or biselenite ($HSeO_3^-$) form (Figure 1). These oxyanions are highly soluble in water and available for uptake by plants (Mikkelsen et al., 1989) and animals (Ohlendorf, 1989). They are also extremely toxic

(Rosenfeld and Beath, 1974), even when present in only trace amounts. A possibility of dealing with excess Se in soils and sediments would be to allow the soil or sediment to become reduced. Flooding those soils or sediments could reduce soluble Se to non-toxic forms and concentrations. Elemental selenium, which is thermodynamically stable over a wide pH and pe range (Fig.2), is insoluble in water and poorly assimilated by micro-organisms (Ohlendorf, 1989) and plants (Mikkelsen et al., 1989). High Fe concentrations and the presence of Se^{2-} in more reduced environments could lead to the formation of ironselenide minerals or Se could be incorporated in ironsulfide minerals (Figures 2-4). Due to their low solubility these mineral phases would limit Se bioavailability.

SUMMARY AND CONCLUSIONS

Interpretations of the biogeochemical behavior of Se in anoxic soils and sediments were made based on equilibrium thermodynamic calculations. pe-pH diagrams were used to display mineral stability in the Fe-S-Se-H_2O system at 25° C and 1 bar total pressure. Constructed phase diagrams indicate that non-toxic elemental Se is stable over a wide pH range and will control Se solubility under moderately reduced conditions. Due to their low solubility ironselenides are important mineral phases limiting Se solubility in anoxic environments, especially under neutral and alkaline conditions. Ironselenides were found to be thermodynamically unstable with respect to their sulfur counterparts. Because both FeS and FeS_2 are abundant and ubiquitous in flooded soils and sediments, these minerals will determine the geochemical and environmental behavior of Se in reducing environments. If we assume that selenide can substitute for sulfide in a solid solution phase,

precipitated FeS will contain an FeSe component. Under conditions of FeS_2 formation, both FeSe and $FeSe_2$ become unstable and elemental Se is produced. Chemical thermodynamics can serve as a qualitative tool in the study of the environmental behavior of Se by predicting stable mineral assemblages in a chemical system containing Se.

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CHAPTER V

SPECIATION AND SOLUBILITY OF ARSENIC AND SELENIUM IN HYCO RESERVOIR (NC) SEDIMENT SUSPENSIONS UNDER CONTROLLED REDOX AND pH CONDITIONS.

ABSTRACT

The influence of sediment redox potential and pH on arsenic and selenium speciation, and solubility was studied. Hyco Reservoir (NC) sediments were equilibrated under controlled redox (500, 200, 0, and -200 mV) and pH (5, natural, and 7.5) conditions. Redox potential and pH affected both speciation and solubility of arsenic and selenium. Under oxidized conditions arsenic solubility was low and 87 % of the arsenic in solution was present as As(V). Upon reduction, As(III) became the major As species in solution, and As solubility increased. Total arsenic in solution increased approx. 25 times upon reduction to -200 mV. No organic arsenicals were detected. In contrast to arsenic, selenium solubility reached a maximum under highly oxidized (500 mV) conditions and decreased significantly upon reduction. Se(VI) was the predominant dissolved selenium species present at 500 mV. At 200 and 0 mV, Se(IV) became the most stable oxidation state of selenium. Under strongly reduced conditions (-200 mV) oxidized selenium species were no longer detectable and selenium solubility was controlled by the formation of elemental selenium and/or metal selenides. Biomethylation of selenium was important under oxidized and moderately reduced conditions (500, 200, and 0 mV). More alkaline conditions (pH 7.5) resulted in both

greater arsenic and selenium concentrations in solution. Dissolved arsenic and selenium increased up to 10 and 6 times, respectively, as compared to the more acidic equilibrations.

INTRODUCTION

Both arsenic (As) and selenium (Se) are subjective to chemically and/or microbiologically mediated oxidation-reduction, and methylation reactions in sediments and natural waters (Cooke and Bruland, 1987; Ferguson and Gavis, 1972; Oremland et al., 1989; Wood, 1974). Because their biotic and abiotic reactivity depends on their physicochemical form (Ferguson and Gavis, 1972; Ohlendorf, 1989), it is important to understand how their interconversions are controlled. One of the most fundamental interactions are redox reactions leading to a transformation of chemical species.

The chemical speciation of As and Se is particularly important in the sediment-water environment. Changes in the sediment environment, i.e., a transition from anaerobic to aerobic conditions or vice versa, may involve a change in chemical species, and thereby alter the environmental behavior of As and Se. In sediment-water environments arsenic can exist in three different oxidation states, arsenate (As(V)), arsenite and monomethyl arsonic acid (As(III)), and dimethyl arsinic acid (As(I)). For selenium, the species of interest are selenate (Se(VI)), selenite (Se(IV), elemental Se (Se(0)), and selenide (Se(-II)). Dimethyl selenide (DMSe) and non volatile organic Se compounds, produced by biomethylation, are also important chemical species of Se.

Numerous studies have dealt with As and Se chemistry in soils and sediments. Adsorption of both elements on soils (Goldberg and Glaubig,

1988a, b; Neal et al., 1987a, b; Neal and Sposito, 1989) and mineral surfaces (Balistrieri and Chao, 1990; Bar-Yosef and Meek, 1987; Pierce and Moore, 1982) have been extensively studied. Soil parameters and biogeochemical processes that affect the mobilization (Ahlrichs and Hossner, 1987; Livesey and Huang, 1981), transport (Alemi et al., 1988), and plant uptake (Baker et al., 1976; Mikkelsen et al., 1989) of As and Se were experimentally investigated. Although the importance of redox status in As and Se chemistry is evident, few studies have investigated the effects of changes in soil or sediment redox status on the environmental behavior of As and Se. Equilibrium thermodynamic calculations have been used to provide qualitatitive information on As (Sadiq et al., 1983) and Se (Elrashidi et al., 1987; Geering et al., 1968) speciation and solubility in soils and sediments. A limited number of experimental studies are available, however, concerning the speciation and solubility of As and Se.

We developed a laboratory experiment that allowed the study of As and Se speciation, and solubilty under controlled redox and pH conditions. The influence of redox potential and pH on the chemical speciation and solubility of As and Se in Hyco Reservoir (NC) sediments is reported here.

MATERIALS AND METHODS

Sediment samples were collected from the Hyco Reservoir, the cooling water source for Carolina Power and Light's Roxboro Steam Electric Plant (Roxboro, NC). The sediment was transported to the laboratory in closed plastic bags. Upon arrival, part of the overlying water was discarded and the sediment was homogenized and stored in a

closed 4-L polyethylene flask until use. X-ray diffraction (Cu Kα radiation) analysis revealed the presence of approx. 65 % of SiO_2 in the sediment. No other crystaline minerals could be identified in bulk powder samples. Kaolinite constituted more than 95 % of the clay fraction.

Sediment suspensions were equilibrated (at 28 ± 2°C) in laboratory microcosms at various redox-pH conditions using the redox-pH control system developed by Patrick et al. (1973). Suspensions were prepared by mixing an amount of sediment equivalent to 150 g of dry weight with d.d. H_2O so that the final sediment to water ratio was 1 to 7.

In a first experiment, sediment suspensions were oxidized (during a 5 day period) until a redox potential of 500 mV was reached, and kept at this redox level for another 10 days. Then, three aliquots were withdrawn, centrifuged [20 min at 7000 rpm, Sorvall GSA-400 rotor, Du Pont CO., Wilmington, DE], and filtered through a 0.45 um micropore filter under an inert argon atmosphere using a pressure-vacuum system (Patrick and Henderson, 1981). One aliquot was used to determine soluble As and Se species. Water soluble sulfides were determined in the second aliquot. Concentrated HNO_3 (200 ul/10 mL) was added to the third aliquot in which selected soluble metals (Ca, Mg, K, Na, Al, Fe, Mn, Cu, Pb, Cd, Ni, and Zn) and total P were determined. The sediment was then allowed to become reduced to 200 mV and the redox potential was maintained at this preselected potential automatically. In the absence of oxygen, chemical and microbial processes caused the redox potential to decrease. Whenever the redox potential dropped below the desired level a small amount of air was pumped into the system to maintain the desired redox potential. The microcosms were continuously purged with oxygen-free

argon gas. Argon gas was effective in purging excesss air at the end of the aeration cycle and in preventing a buildup of gaseous decomposition products such as carbon dioxide and hydrogen sulfide. Using this system, we could maintain the desired redox potential within ± 20 mV. After 10 days of equilibration at a redox level of 200 mV, the sampling procedure was repeated and the soluble As, Se, metals, and sulfides determined. Further stepwise reductions of the sediment redox potential were carried out in a similar manner to levels of 0 mV and -200 mV, respectively. After 10 days of incubation at the preselected redox levels, sediment suspensions were sampled and analyzed for soluble As, Se, metals and, sulfides. Reduction of the sediment suspension led to an increase in pH. At the end of each equilibration period the pH was 4.0 for 500 mV, 5.3 for 200 mV, 6.1 for 0 mV, and 6.9 for -200 mV, respectively. The experiment was run in duplicate.

In a second set of experiments similar sediment suspensions were equilibrated under controlled redox and pH conditions. The following redox-pH combinations were selected: redox, -200, 0, 200, and 500 mV; pH 5, and 7.5. The suspension pH was manually adjusted by additions of 2 M HCl or NaOH, as required, to bring the pH to the desired value. Redox potentials were maintained at the preselected levels automatically, as described above. The microcosms were sampled after 25 days of equilibration. Arsenic and selenium species, and metals in solution were determined. The equilibrations were run in duplicate. Upon acidification of the sediment to pH 5, strongly reducing conditions (-200 mV) could not be achieved, and results are therefore not available.

All extracts were analyzed for Se and As species within 4 h after sampling. The As species analyzed for in the water extracts were:

inorganic As(III), As(V) and, monomethylarsonic acid (MMAA) and dimethylarsenic acid (DMAA) species. Selenium(VI), Se(IV), Se(-II,0), dimethyl selenide (DMSe), and oxidized methylated Se compounds (Ox.MSe) were determined in the extracts. Oxidized methylated Se compounds represent those organoselenium compounds (e.g. dimethyl selenone, methaneselenic acid) that are reduced by $NaBH_4$ to their corresponding methylated selenide derivatives (Cooke and Bruland, 1987). It should be noted that the nomenclature of As(III) represents the sum of all the species that contain the AsO_3^{3-} species (e.g. H_3AsO_3, $H_2AsO_3^-$, $HAsO_3^{2-}$, and AsO_3^{3-}), likewise for As(V) and the Se species. Both As and Se species were determined with a hydride generation/ trapping/ separation apparatus followed by atomic absorption spectrophotometer detection. Details of the analytical techniques used in our laboratory for As and Se speciation in sediment-water extracts were reported earlier (Masscheleyn et al., 1990, 1991). Several samples were analyzed by the standard additions technique. No interferences in the analysis of As and Se species were found.

Metals, major cations and P in solution were determined with a Jarrel-Ash ICP (Atom Comp series 800, Waltham, MA). Sulfide was measured with an ion-specific Ag/S electrode in an anoxic buffer solution (sulfide operating instruments; Lazar Research Laboratories, Los Angeles, CA). Statistical analyses were done using the PROC CORR and PROC GLM procedures of the Statistical Analysis System (1985).

RESULTS AND DISCUSSION

Arsenic speciation and solubility as affected by sediment redox potential and pH.

Figure 1A shows the species distribution of arsenic at the four redox levels studied in the uncontrolled pH experiment. Under oxidized conditions (500 mV), arsenic solubility was low and 87 % of the As in solution was present as As(V). Upon reduction, As(III) became the major dissolved As species, and As solubility increased substantially. Greatest As concentrations in solution were found at -200 mV, the most reduced condition studied. Total As in solution increased approx. 25 times upon reduction of the sediment suspension from 500 mV to -200 mV. Although thermodynamically unstable, there was a considerable amount of As(V) present under reduced conditions indicating that chemical kinetics play an important role in the conversion of As(V) to As(III). At -200 mV, As(V) comprised 18 % of the total soluble As.

Results obtained for the equilibrations under controlled redox conditions at pH 5.0 (Figure 1B) were comparable to those obtained during the uncontrolled pH experiment. However, a more alkaline pH (7.5) had a major effect upon both the levels and chemical forms of dissolved As. At pH 7.5 (Figure 1C) arsenic solubility increased significantly under both oxidized and moderately reduced conditions (500, 200 and 0 mV) as compared to the more acidic (Figure 1A and 1B) equilibrations. Under alkaline conditions (pH 7.5) and redox potentials of 500, 200, and 0 mV, As(V) was the major dissolved As species. Upon further reduction, As(III) constituted approx. 85 % of the total soluble As.

The drastic increase of As observed upon reduction is probably linked to the reductive dissolution of iron oxyhydroxides. Calculations

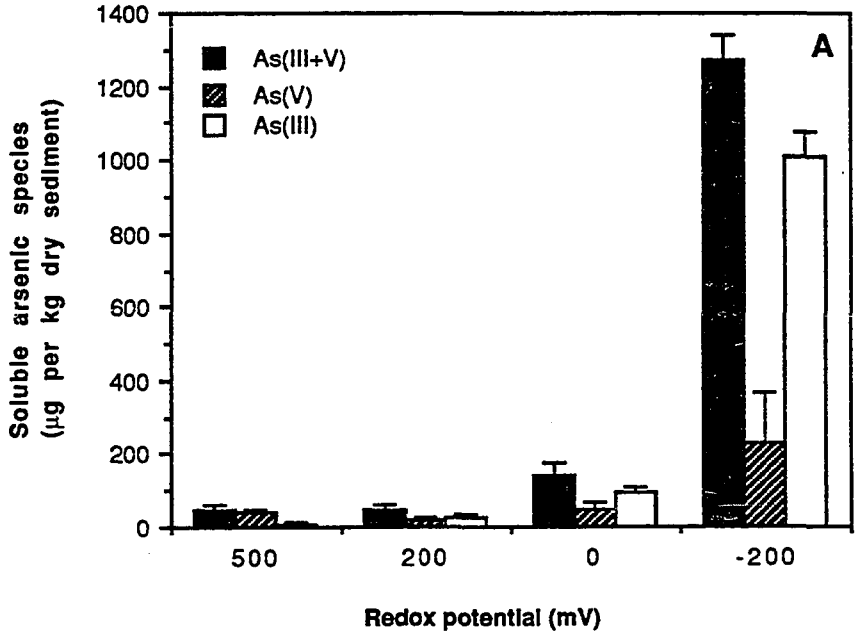

Figure 1: Distribution of soluble arsenic species under controlled redox and pH conditions. A) Equilibrations at natural pH (4.0 for 500 mV, 5.3 for 200 mV, 6.1 for 0 mV, and 6.9 for -200 mV).

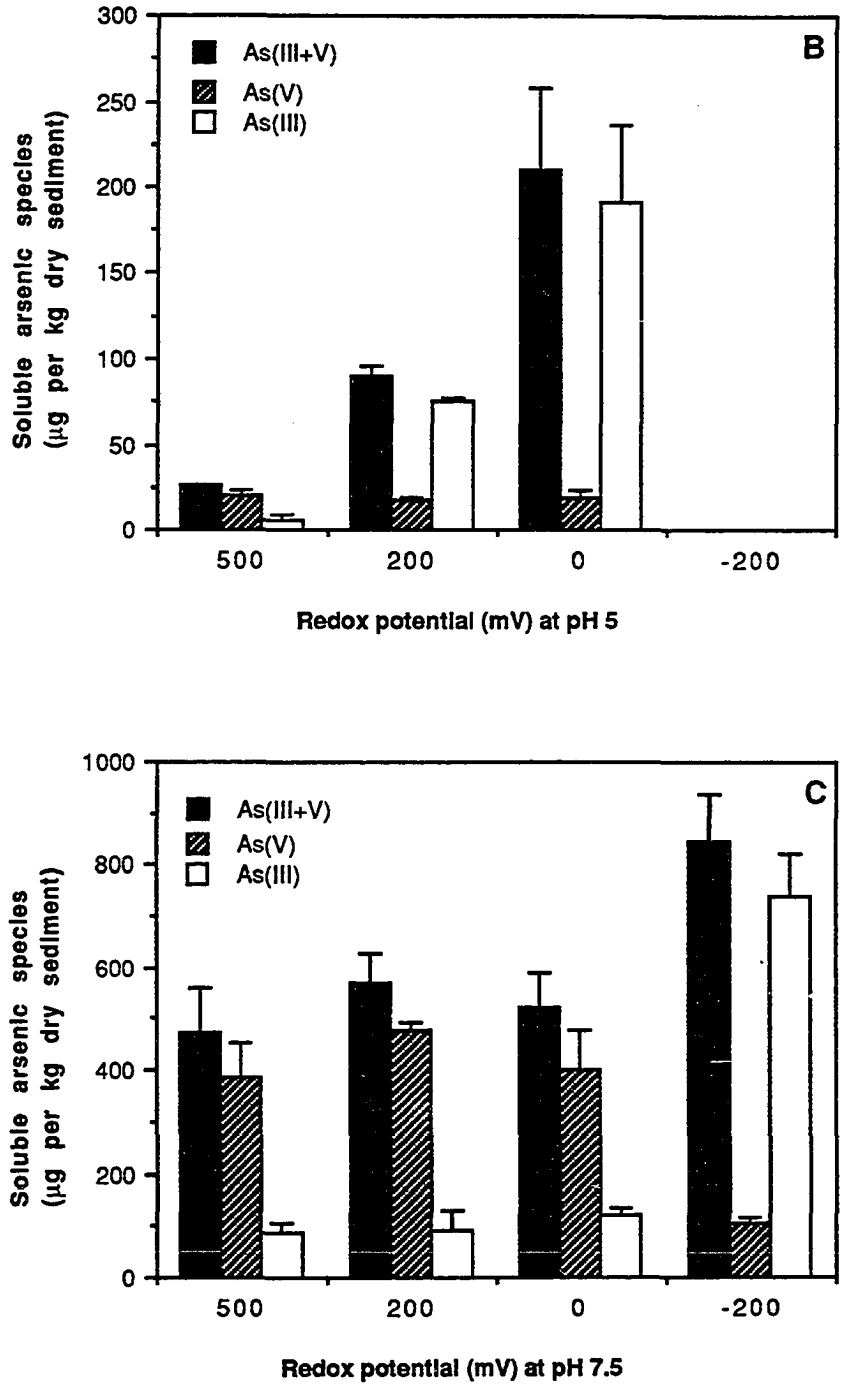

Figure 1: Distribution of soluble arsenic species under controlled redox and pH conditions. B) Equilibrations at pH 5.0. C) Equilibrations at pH 7.5. Note changes in scale.

performed with the computer program GEOCHEM (Sposito and Mattigod, 1979) showed the suspensions to be several orders of magnitude undersaturated with respect to $FeAsO_4$, $AlAsO_4$, $Mn_3(AsO_4)_2$, and $Ca_3(AsO_4)_2$ indicating that precipitation-dissolution reactions of As minerals were not controlling As solubility in the sediment suspensions. Arsenic chemistry in soils and sediments is believed to be controlled by adsorption-desorption mechanisms (Livesey and Huang, 1981). Soil pH (Goldberg and Glaubig, 1988b), the amount and type of clay (Bar-Yosef and Meek, 1987) and iron oxides (Livesey and Huang, 1981; Pierce and Moore, 1982) have been implicated in the sorption of As. Dissolution of iron oxyhydroxides upon reduction and subsequent release of adsorbed As would lead to increased dissolved As concentrations. In our experiments, total water soluble As and Fe were highly correlated ($P < 0.01$) suggesting the importance of iron oxyhydroxides in controlling As adsorption-desorption reactions. The increasing negative surface charge of the oxides with increasing pH facilitated desorption of As(V), as was illustrated by the higher soluble As concentrations at pH 7.5. The absence of correlation between soluble Al, Mn and As indicated that Al and Mn-oxides were less important in controlling As solubility. Although not directly evident from this experiment, the transformation of As(V) to As(III) could have been an additional mechanism leading to increased As concentrations in solution. Under the redox-pH conditions encountered in this study, As(V), if present, will be negatively charged (as $H_2AsO_4^-$ or $HAsO_4^{2-}$) and readily adsorbed to positively charged amorphous iron oxyhydroxide surfaces. Upon reduction, however, As(III) will be present predominantely as the uncharged H_3AsO_3 species, enhancing desorption.

Upon reduction of the sediment suspensions to -200 mV soluble sulfide levels up to 28 mg L^{-1} were measured. Concentrations of water soluble Zn, Cu, and Ni decreased 20, 12, and 5 times, respectively, as compared to dissolved concentrations at 500 mV (Table 1), suggesting the formation of insoluble metal sulfides. Soluble concentrations of Cd and Pb were below the detection limit of the ICP and are therefore not included. Although As(III) has been reported to have strong affinity for S (Ferguson and Gavis, 1972), results indicated that As solubility was not limited by the formation of insoluble arsenic sulfide minerals, such as orpiment (As_2S_3) or arsenopyrite (FeAsS). Phosphorus solubility increased upon reduction of the sediments and, as with As, water soluble P concentrations were significantly correlated with the concentrations of Fe in solution.

Although our analytical technique was optimized for the determination of methylarsonic acid and dimethylarsinic acid, we were not able to detect soluble organic arsenicals in the sediment suspensions.

Selenium speciation and solubility as affected by sediment redox potential and pH.

Figure 2 summarizes the effect of redox potential and pH on selenium speciation and solubility in sediment suspensions. Selenium solubility and the dominant Se species found at 500, 200, 0, and - 200 mV in the uncontrolled pH experiment are shown in Figure 2A. In contrast to arsenic, selenium solubility was greatest under oxidized (500 mV) conditions and decreased significantly ($P < 0.01$) upon reduction of the sediment suspensions. Furthermore, the presence of methylated selenium

Table 1: Concentration of dissolved Fe, Mn, Al, Cu, Ni, Zn, and P in Hyco Reservoir sediment suspensions under controlled redox potentials.

Redox	pH	Fe	Mn	Al	Cu	Ni	Zn	P
(mV)		<----------		mg kg^{-1}	dry	sediment		---------->
500	4.0 ±0.3	3.18† ±0.49§	221 ±43	5.81 ±0.19	2.71 ±0.17	1.47 ±0.19	15.6 ±1.47	1.08 ±0.15
200	5.3 ±0.2	3.69 ±1.03	269 ±15	2.46 ±0.67	0.73 ±0.05	1.19 ±0.39	10.6 ±1.83	1.05 ±0.35
0	6.1 ±0.2	732 ±48	450 ±46	2.20 ±0.24	0.21 ±0.09	0.56 ±0.09	4.58 ±2.03	1.85 ±0.34
-200	6.9 ±0.1	1064 ±134	458 ±15	2.10 ±0.49	0.22 ±0.06	0.27 ±0.04	0.56 ±0.10	4.06 ±0.89

† Mean of duplicate equilibrations

§Standard deviation

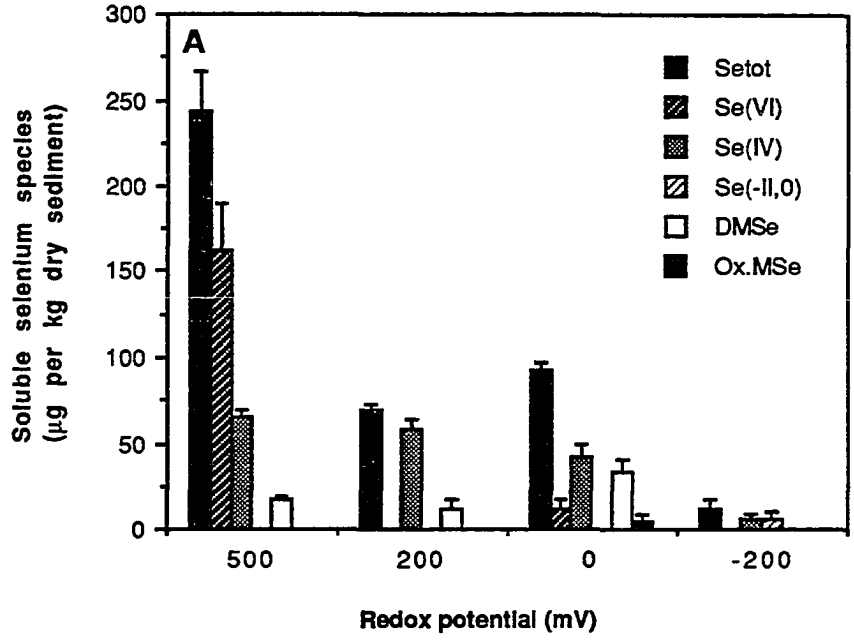

Figure 2: Distribution of soluble selenium species under controlled redox and pH conditions. A) Equilibrations at natural pH (4.0 for 500 mV, 5.3 for 200 mV, 6.1 for 0 mV, and 6.9 for -200 mV).

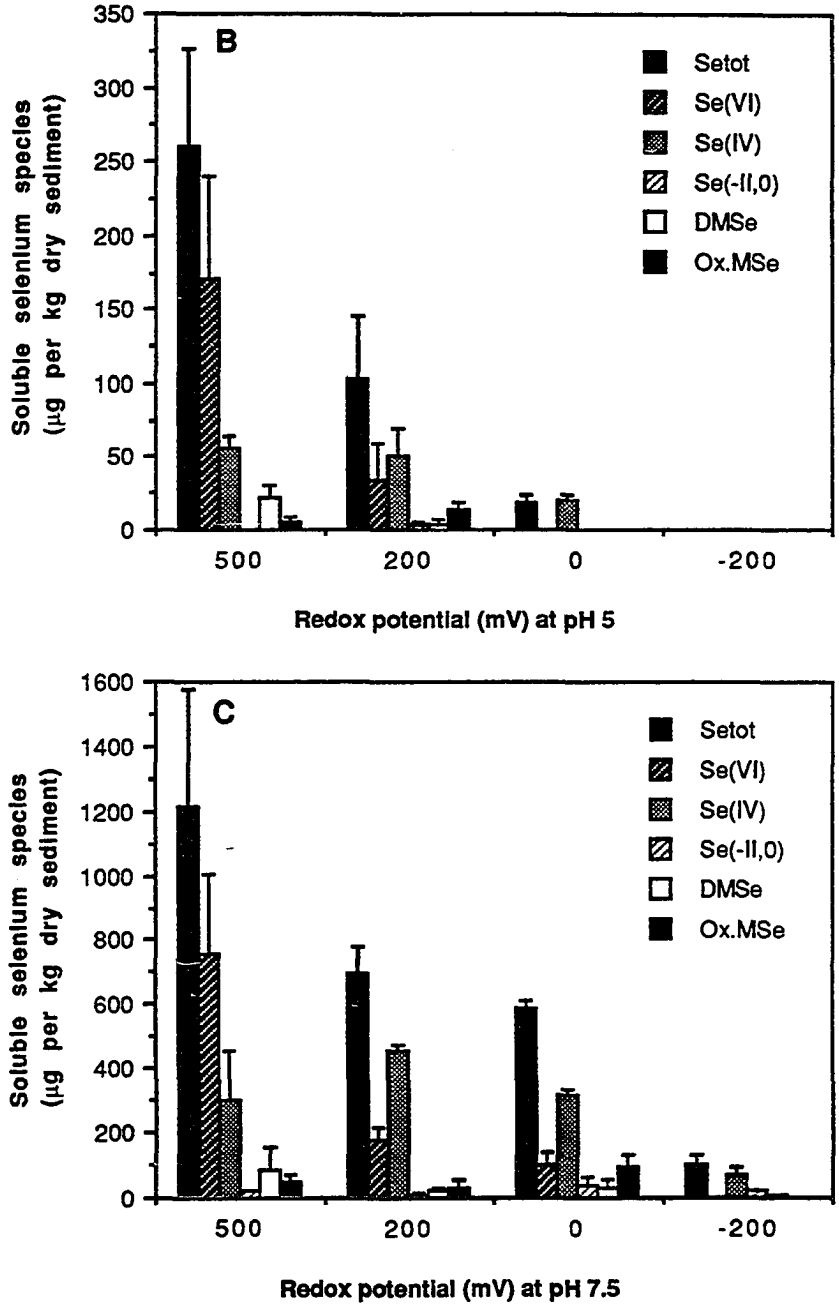

Figure 2: Distribution of soluble selenium species under controlled redox and pH conditions. B) Equilibrations at pH 5.0. C) Equilibrations at pH 7.5. Note changes in scale.

species suggest that Se chemistry was dominated by chemical transformations between both inorganic and organic species.

Under highly oxidized conditions (500 mV) selenium solubility reached a maximum. Both Se(VI) and Se(IV) were present, although Se(VI) is the only thermodynamically stable form. Reduction of the sediment suspensions led to transformations of Se species and a decrease in dissolved Se concentrations. At 200 and 0 mV, Se(IV) was the most stable oxidation state of Se. At -200 mV, Se(VI) was no longer detectable and Se(IV) concentrations decreased. A barely detectable amount of Se(-II,0) was observed under strongly reduced conditions (-200 mV). Methylated Se compounds were present at 500, 200, and 0 mV. Dimethyl selenide constituted from 5 to 36 % of the total soluble Se concentration, depending on the redox status. Oxidized methylated Se compounds (Ox.MSe) were present in only minor amounts.

The concentrations of water soluble Se were also found to be pH dependent (Figure 2B and 2C). As with arsenic, an increase in pH led to increased dissolved Se concentrations. Under oxidized (500 mV) and moderately reduced conditions (200 and 0 mV) selenium solubility was as much as 6 times higher at pH 7.5 than in the equilibrations at pH 5. At pH 7.5, both Se(IV) and Se(-II,0) were detected at -200 mV. Sediment suspensions were found to be undersaturated with respect to both metal-selenite and metal-selenate minerals. In a recent study, Elrashidi et al. (1987) reported metal-selenite and ,in particular, metal-selenate minerals to be too soluble to persist in soils and sediments. Under oxidized conditions Se solubility is controlled by adsorption-desorption reactions. Adsorption of Se(IV) and Se(VI) species has been extensively studied (Goldberg, 1988a; Neal et al., 1987a, b; Neal and Sposito,

1989). It has been consistently shown that Se(IV) adsorption decreases with increasing pH in the range 4-9 and that Se(VI) adsorption is minimal under most pH conditions. Both Fe and Mn oxides sorb Se(IV), with Fe oxides sorbing more (Balistrieri and Chao, 1990). In our experiments, a pH increase from 5.0 to 7.5 led to greater dissolved Se(IV) and Se(VI) concentrations. The increase in Se(IV) at higher pH is probably caused by its pH dependent adsorption-desorption behavior. Higher dissolved Se(VI) levels can be explained by increased oxidation rates (Se(IV) -> Se(VI)) with increasing pH.

The decrease in total soluble Se and the disappearance of dissolved oxidized Se species upon reduction of the sediment suspensions clearly illustrate that selenium solubility under anaerobic conditions is controlled by the formation of insoluble elemental Se and / or metal selenides. Unfortunately, the present analytical techniques are not able to distinguish between elemental Se or selenides in solution. Redox-pH diagrams showing the predominance areas for dissolved Se species under earth surface conditions have been recently constructed (Neal et al., 1987a; Mayland et al. 1989). The phase diagrams indicate that under reducing conditions elemental Se is stable over a wide pH range. Under strongly reducing conditions H_2Se or HSe^- would be thermodynamically preferred. However, it was illustrated by Elrashidi et al. (1987) that, due to their low solubility, metal selenides may form at higher redox than that required for the formation of elemental Se. Their calculations indicated that elemental Se would form only after the exhaustion of metals like Pb^{2+}, Cu^{2+}, and Cd^{2+} in solution. Furthermore, metal selenides are thermodynamically less soluble than their sulfur counterparts (Table 2) and should therefore form first. Although metal

Table 2: Solubility products for selected metal sulfides and metal selenides at 25°C and 10^5 Pa.

Mineral	Reaction products	-log K_{sp}	Reference
α-FeS	$Fe^{2+} + S^{2-}$	16.21	Lindsay (1979)
FeSe	$Fe^{2+} + Se^{2-}$	26.00	Elrashidi et al. (1987)
α-ZnS	$Zn^{2+} + S^{2-}$	24.70	Lindsay (1979)
ZnSe	$Zn^{2+} + Se^{2-}$	29.40	Elrashidi et al. (1987)
PbS	$Pb^{2+} + S^{2-}$	27.51	Lindsay (1979)
PbSe	$Pb^{2+} + Se^{2-}$	42.10	Elrashidi et al. (1987)
CuS	$Cu^{2+} + S^{2-}$	36.10	Lindsay (1979)
CuSe	$Cu^{2+} + Se^{2-}$	48.10	Elrashidi et al. (1987)

selenide formation could be kinetically inhibited, the formation of insoluble metal sulfides upon reduction (Table 1) suggests that Se solubility under anaerobic conditions could have been controlled by metal selenide formation.

It is also important to recognize that the amount of methylated selenium reported here is a measure of the net result of two opposing processes: methylation and demethylation. Both processes probably occur at the same time but there is no effective way of separating methylation from demethylation in sediments. It further seems reasonable to assume that selenium was methylated by the microorganisms as a means of detoxification since methylated selenium compounds were only detected when soluble Se was high. Organisms from very different groups like aerobic and anaerobic bacteria and fungi (Doran, 1982; Zieve et al., 1984) with the capacity to methylate Se have been identified. Our results, obtained at precisely controlled redox potentials, show that the oxidation status of the sediment is another important factor influencing Se methylation. Methylation of Se and the persistence of the methylated selenium compounds formed were both favored under oxidized and moderately reduced conditions (500, 200, and 0 mV) as compared to strongly reduced conditions (-200 mV).

SUMMARY AND CONCLUSIONS

Redox potential and pH affected both speciation and solubility of arsenic and selenium in Hyco Reservoir (NC) sediment suspensions. Under highly oxidized conditions (500 mV) arsenic solubility was low and 87 % of the As in solution was As(V). Upon reduction, As(III) became the major As species in solution, and As solubility increased substantially.

Results suggest that As solubility was controlled by reductive dissolution of iron oxyhydroxides. In contrast to arsenic, selenium solubility reached a maximum under highly oxidized (500 mV) conditions and decreased significantly upon reduction. Se(VI) was the predominant dissolved selenium species present at 500 mV. At 200 and 0 mV, Se(IV) became the most stable oxidation state of selenium. Under strongly reduced conditions (-200 mV) oxidized selenium species were no longer detectable and selenium solubility was controlled by the formation of elemental selenium and/or metal selenides. Biomethylation of selenium was important under oxidized and moderately reduced conditions. More alkaline conditions (pH 7.5) led to greater dissolved As and Se concentrations, as compared to the more acidic equilibrations.

ACKNOWLEDGEMENTS

We thank Mr. Steve Woock from Carolina Power and Light (New Hill, NC) for collecting and providing the sediments used in this study.

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CHAPTER VI

SPECIATION AND REDOX CHEMISTRY OF ARSENIC IN A CONTAMINATED SOIL

ABSTRACT

Based on experimental data and equilibrium thermodynamic calculations, evidence is presented for the mechanisms controlling arsenic solubility in a contaminated soil. Adsorption-desorption reactions and coprecipitation of As(V) with amorphous iron oxyhydroxides determined As solubility. At higher redox levels, As solubility was controlled by adsorption-desorption reactions. An alkaline pH or, the reduction of As(V) to As(III) and simultaneous desorption, released substantial proportions of As into solution. Under moderately reduced conditions (0-100 mV) arsenic solubility was controlled by the dissolution of iron oxyhydroxides. Data suggest that a major part of arsenic was coprecipitated [as As(V)] with the iron oxyhydroxides. The observed slow kinetics of the As(V)-As(III) transformation and high concentrations of Mn present make the precipitation of a $Mn_3(AsO_4)_2$ phase under reduced conditions possible. Alterations in the oxidation state of As, as influenced by redox potential and pH, greatly affected its solubility in soil.

INTRODUCTION

Because the solubility, mobility, bioavailability, and toxicity of arsenic (As) depends on its oxidation state (Brannon and Patrick, 1987; Deuel and Swoboda, 1972; National Research Council, 1977; U.S. EPA, 1976), studies of As speciation and transformations among species are essential to understanding the As behavior in the environment. Arsenate [As(V)] and arsenite [As(III)] are the primary As forms in soils. Both As(V) and As(III) are subjected to chemically and/or microbiologically mediated oxidation-reduction and methylation reactions in soils and natural waters (Braman and Foreback, 1973; Brannon and Patrick, 1987; Ferguson and Gavis, 1972; Johnston, 1978). Numerous studies have dealt with As sorption on specific minerals and soils. Amorphous Fe and Al hydroxides (Pierce and Moore, 1982; Sakata, 1987), clay content (Elkhabit et al., 1984), and pH (Elkhabit et al., 1984; Pierce and Moore, 1980, 1982; Sakata, 1987) are the soil properties reported to be most related to As sorption. Methylated As oxyacids can be produced by a variety of micro-organisms and their presence has been reported in a wide range of natural waters (Andreae and Klumpp, 1979; Braman and Foreback, 1973), soils and sediments (Johnston, 1978; Woolson, 1975).

Although of great environmental importance, little detailed information is available about the influence of redox potential on the behavior of As in contaminated soils. Deuel and Swoboda (1972) reported an increase of total soluble As under reduced conditions and attributed this increase to the reduction of ferric arsenate compounds. Using an equilibrium thermodynamics approach, Sadiq et al. (1983) developed solubility isotherms for several metalarsenates. Under oxidized conditions, they predicted that As solubility would be determined by a

$Ca_3(AsO_4)_2$, $Mn_3(AsO_4)_2$ or a $Pb_3(AsO_4)_2$ phase. Similar conclusions were reported by Hess and Blanchar (1976). Under reducing conditions, arsenite minerals are too soluble to persist in soils, but arsenic sulfides were predicted to be stable (Sadiq et al., 1983). Livesey and Huang (1981) concluded that soluble arsenate was controlled by adsorption reactions in soils, rather than through the precipitation of arsenate compounds.

The purpose of this paper is to report the effect of soil redox potential and pH on the speciation and solubilty of As in a contaminated soil. Interpretations were based on results of laboratory experiments and simple equilibrium thermodynamic calculations. Although conclusions are based on experiments with one particular soil, they provide valuable information to those dealing with As contaminated soils and industrial or municipal wastes contaminated with As.

MATERIALS AND METHODS

Soil

A soil known to be contaminated with As was collected near Kolin, Louisiana (USA). The soil had been exposed to As contamination for a period of greater than 20 years. A detailed description of the sampling site was given by Kotuby-Amacher and Gambrell (1988). Surface (0-20 cm) samples were taken from the soil, belonging to the Acadia-Kolin Association [Aeric Ochraqualf]. Upon arrival in the laboratory, the soil was air-dried, ground to pass a 1 mm sieve, homogenized by thorough mixing, and stored in 4-L polyethylene flasks until use.

Experiments

In a first experiment, 60-g portions of dry soil were placed in a set of plastic canisters (Jugsujinda et al., 1987), and gently compacted with intermittent additions of distilled deionized water followed by incubation under flooded conditions for a desired period of time. The saturated soil created a 6 cm deep layer in the core. Then, water was introduced from the bottom with the help of a syringe and needle until an overlying floodwater depth of about 2 cm was created. Adding water from the bottom helped to release entrapped air. To insure reducing conditions the canisters were sealed with the supplied caps. Duplicate canisters were opened after 1, 3, 15, 35, 65 and 105 days of submergence. An Eh-pH depth profile was taken using a system similar to that described by Patrick and Delaune (1972). Rather than measuring continuous profiles, we decided to gradually lower the micro-electrodes to preselected depths (0.25, 0.5, 1.5, 2.5, 3.5, and 4.5 cm). Preliminary experiments had shown that an equilibration period of 4 hrs was necessary to obtain constant redox readings. After an Eh-pH depth profile was taken, the overlying water was removed from the cores with a plastic syringe followed by horizontal sectioning at 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 cm core depths. The volume (0.5-0.8 mL) of saturation extracts, recovered from soil sections by centrifugation and filtration, was not sufficient for the determination of all elements of interest. Therefore, each section was immediately transferred to a 40-mL polycarbonate centrifuge tube to which a known volume of oxygen free d.d. water was added. The lids of the centrifuge tubes were equipped with rubber septa which facilitated the displacement of air with argon. The soil suspensions were shaken for 1 hr on a mechanical shaker,

centrifuged [20 min at 7000 rpm, Sorvall GSA-400 rotor, Du Pont CO., Wilmington, DE] and filtered through a 0.45-uM micropore filter under an inert argon atmosphere using a pressure-vacuum system (Patrick and Henderson, 1981). Each supernatant was divided into two aliqouts. One was used for the determination of soluble As species and sulfides. Concentrated HNO_3 (200 ul/10 mL) was added to the second aliquot in which selected soluble metals (Ca, Mg, K, Na, Al, Fe, Mn, Cu, Pb, Cd, Ni, and Zn) and total P were determined. After the extraction, the dry weight of the soil in each tube was determined. This allowed the calculation of the soil to water ratio, which varied from 2.70 to 3.40.

In the next series of experiments, soil suspensions were equilibrated under controlled redox and pH conditions. The soil was equilibrated (at 28±2 °C) in laboratory microcosms at various redox-pH conditions using the pH-redox control system developed by Patrick et al. (1973). Suspensions were prepared by mixing an amount of soil equivalent to 200 g of dry weight with d.d. water so that the final soil water ratio was 1 to 6. The following redox-pH conditions were used: redox - 200, 0, 200, and 500 mV; pH 5, pH 8, and uncontrolled. In the uncontrolled pH experiments, the microcosms were sampled at 3-day intervals over a 24-day period. The other microcosms were sampled at the end of the 24-day equilibration period. Natural (uncontrolled) pH values at the end of the incubation period were 5.2 for 500 mV, 6.7 for 200 mV, 7.0 for 0 mV, and 7.2 for -200 mV. All experiments were run in duplicate.

Sampling proceeded as follows. Two soil suspension aliquots were withdrawn from each microcosm, centrifuged, and filtered through a 0.45-μM micropore filter under an inert argon atmosphere for reduced

treatments. One filtered supernatant was used for the determination of As and sulfides, the other was treated as described above and used for cation and metal analysis.

Analysis

The water extracts were analyzed for As species [As(III) and, As(V)] with a pH selective hydride generation/separation technique followed by atomic absorption spectrophotometry detection. The system is similar to that previously used for selenium speciation in our laboratory (Masscheleyn et al., 1990). The arsines from inorganic As(III) were selectively generated and purged for analysis from a solution buffered at pH 6.5 with Tris (tris (hydroxymethyl) aminomethane) buffer (Andreae, 1977; Johnston, 1978). The solution was then further acidified with conc. HCl (to a final concentration of 2 M HCl) and analyzed for As(V) (Masscheleyn et al., 1991). Although our analytical technique was optimized for the determination of monomethylarsonic acid, and dimethylarsenic acid in the presence of large concentrations of inorganic As species, we were not able to detect any organic arsenicals present. The performance of the analysing step involving hydride generation, cryogenic condensation and volatilization was assessed by analysis of EPA water quality reference standards for total inorganic As [As(III)+As(V)] and yielded values of 25 and 241 ug L^{-1} compared with the true values of 26.7 and 235 ug L^{-1}. Absorbance was found linear over the range 2 - 120 ng As and had a sensitivity of 0.0083 absorbance units/ng As. Six measurements of absorbance at the 50 ng level gave a relative standard deviation of 2.3 %. All As species in the extracts were analyzed within 5 h after sampling.

Metals, major cations and total P in solution were analyzed with a Jarrel Ash ICP. The performance of the ICP was checked with EPA reference samples. Sulfide was measured by an ion-specific Ag/S electrode in an anoxic buffer solution (sulfide electrode operating instruments; Lazar Research Laboratories, Los Angeles, CA) and titration alkalinity determinations were used to estimate the concentrations of soluble carbonate species.

Total As content of the soil was determined after Aqua Regia digestion. X-ray diffraction (Cu Kα radiation) was used to study the mineralogy of bulk powder and clay size soil samples. Statistical analysis were preformed with PC-SAS (Statistical Analysis System, 1985).

RESULTS AND DISCUSSION

Arsenic speciation, transformations and solubility as affected by soil redox potential.

The soil contained large amounts of SiO_2 (> 90%) associated with minor concentrations of both K-feldspars and plagioclase minerals. Kaolinite and mixed layered Illite-Montmorrilonite constituted more than 85 % of the clay fraction. No crystalline As minerals were detected using the X-ray diffraction technique. Using selective extraction techniques, Kotuby-Amacher and Gambrell (1988) determined the Mn oxide, and amorphous Fe oxide content of the surface soil to be in the order of 0.03 and 0.15% respectively. The soil had a total As content of 555 $\pm$ 18 mg kg^{-1} (n=5) dry soil. Correlation analysis revealed that the major part of the As present was associated with the amorphous Fe oxide phase (Kotuby-Amacher and Gambrell, 1988).

The predicted effect of redox potential (Eh) and pH on the oxidation state of As is summarized in Figure 1, which was constructed using critically evaluated thermodynamic data (Dove and Rimstidt, 1985; Lindsay, 1979). It can be seen that H_3AsO_3, $H_2AsO_4^-$, $HAsO_4^{2-}$, or $As_{(s)}$ will be the dominant As species present in a soil, depending on its Eh and pH. It is important to remember that this Eh-pH diagram is really a "predominance-area" diagram because the outlined fields are those areas containing where the designated species make up more than 50% of the total concentration. To make the diagram more useful, the redox couples $Fe(OH)_3$/Fe(II) and MnO_2/Mn(II) were also included. Changing Eh-pH conditions during the experiments can easily be followed on the graph. Since both Mn and Fe oxides and hydroxides exist in various degrees of crystallinity (amorphous, meta-stable poorly crystalline, and crystalline), the actual stability fields for these compounds may differ from computed boudaries from soil to soil.

In the first experiment, a time-series evaluation between Eh, pH, soluble redox elements, and As species in soil cores was made. Changes in vertical distribution of Eh, As(III), As(III+V), Mn, and Fe upon flooding are presented in Figure 2. During the equilibration under submerged conditions, the pH increased from 5.6 to 7.1. Little variation in pH ($\pm$ 0.2) was found throughout a particular profile. Flooding periods longer than 35 days did not significantly alter the vertical distribution of Eh and redox elements studied. Flooding (reducing conditions) of the soil did not have an influence on soluble Al, Ca, Mg, Na and K concentrations. However, as early as three days after flooding, there was a considerable increase in reduced Mn throughout the soil core. As the incubation period increased and more reducing conditions

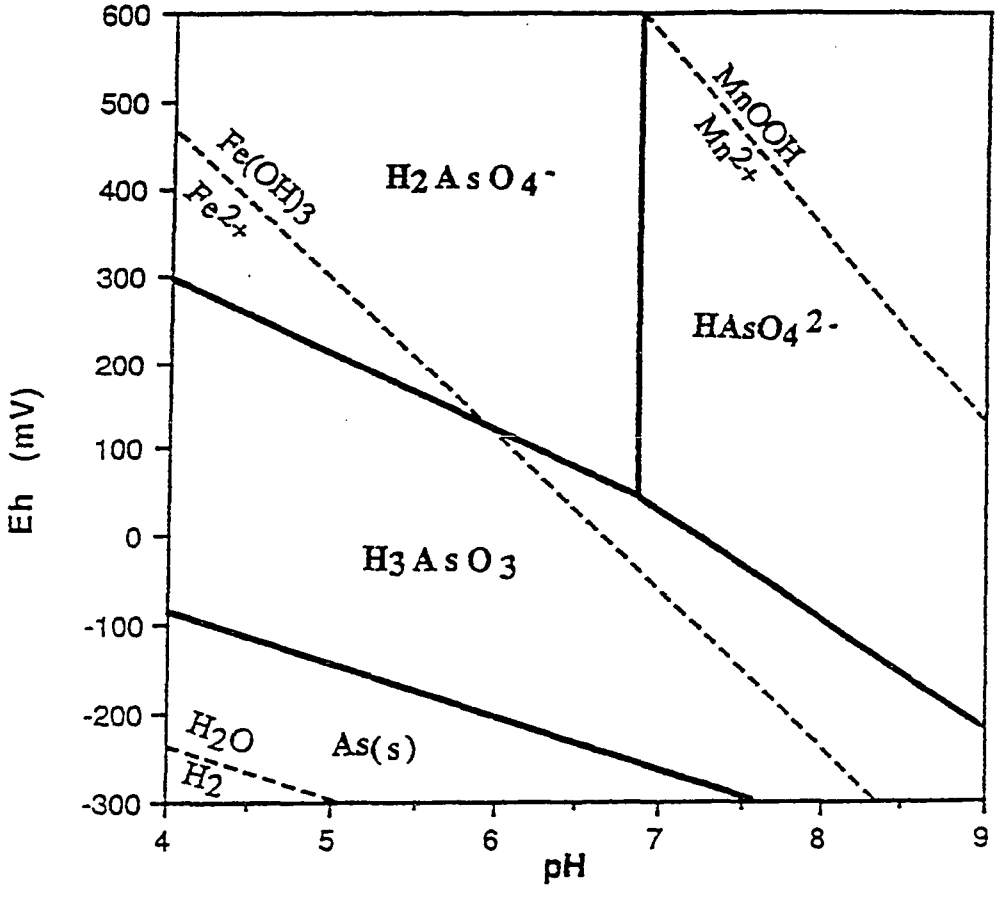

Figure 1: Eh-pH diagram for the system As-H_2O. Activities of As, Mn and Fe were all taken to be 10^{-4}.

(Eh <150 mV) developed, dissolved Mn increased to a near constant value of approximately 35 mg kg^{-1} soil. No iron was reduced after three days of flooding. When, between the 15th and 35th day of submergence, redox levels dropped below 100 mV, soluble iron concentrations reached a maximum and stayed unchanged for the rest of the incubation period. Interesting information about As speciation and solubility was obtained when changes in vertical distributions of Eh, Mn, Fe, and As species (Figure 2A-2D) were compared. Some arsenic was reduced and released into solution before the reduction of the ferric hydroxide layer. Differences in depth profiles presented in figures 2A and 2B clearly illustrate this. While soluble Fe concentrations remained unchanged, dissolved As concentrations increased by a factor of two and, As(III) became the major species present. Although not evident from this experiment, the reduction of Mn probably preceeded the As reduction as would be expected from thermodynamic calculations (Figure 1). Upon longer incubation, a sharp and correlative increase [$P<0.01$] of total As [As(III)+As(V)] and Fe was observed throughout the soil core. When expressed on molar basis, the dissolution of As occured at Fe to As ratio's varying from 0.8 to 1.7.

Generally, observed increases in soluble As upon reduction have been attributed to the reduction of ferric arsenate and other forms of iron combined with arsenic (Aggett and O'Brien, 1985; Aggett and Roberts, 1986; Deuel and Swoboda, 1972; Seyler and Martin, 1989). From our experiment, however, it can be seen that the reduction and release of As may occur before the dissolution of iron oxyhydroxides. Apparently, the dissolution of the ferric hydroxide layer led to a

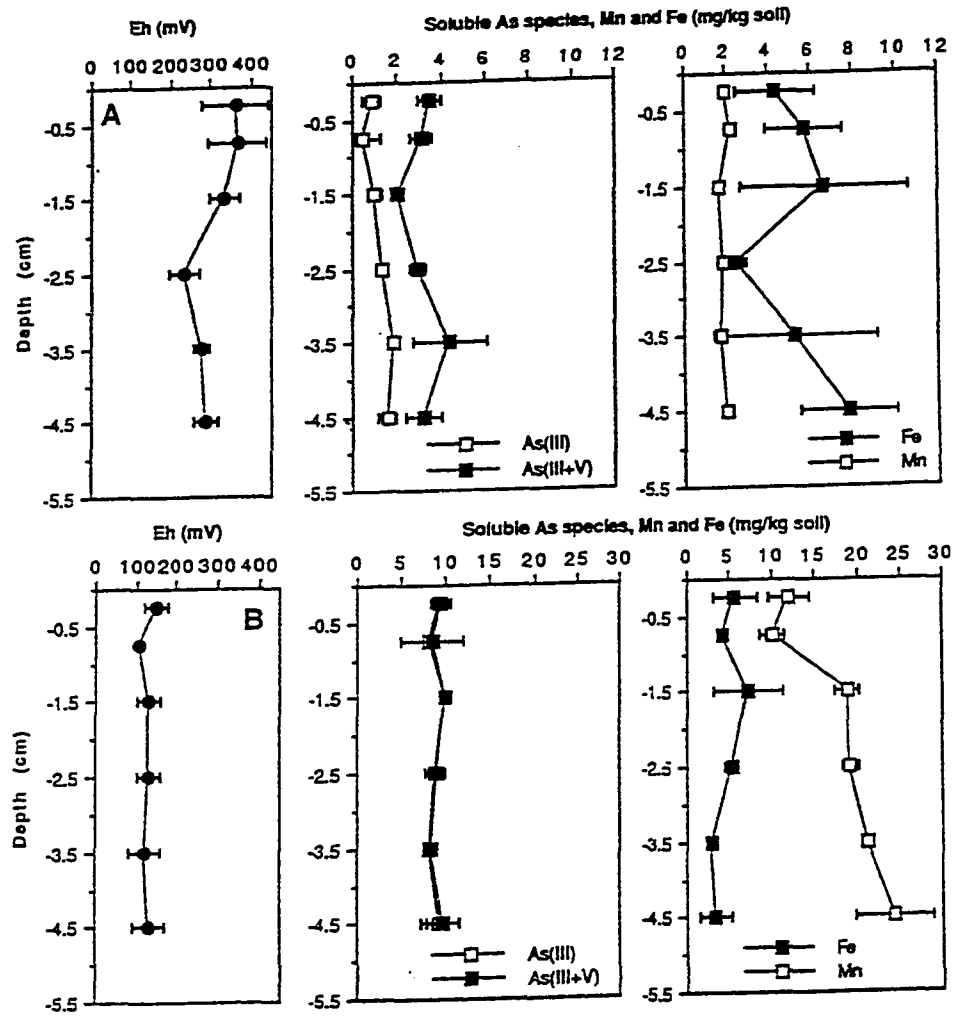

Figure 2: Vertical distribution of Eh, soluble As species, Mn and Fe. A) after 1 day of flooding (pH = 5.7 $\pm$ 0.1). B) after 3 days of flooding (pH = 6.4 $\pm$ 0.2). Note changes in scale.

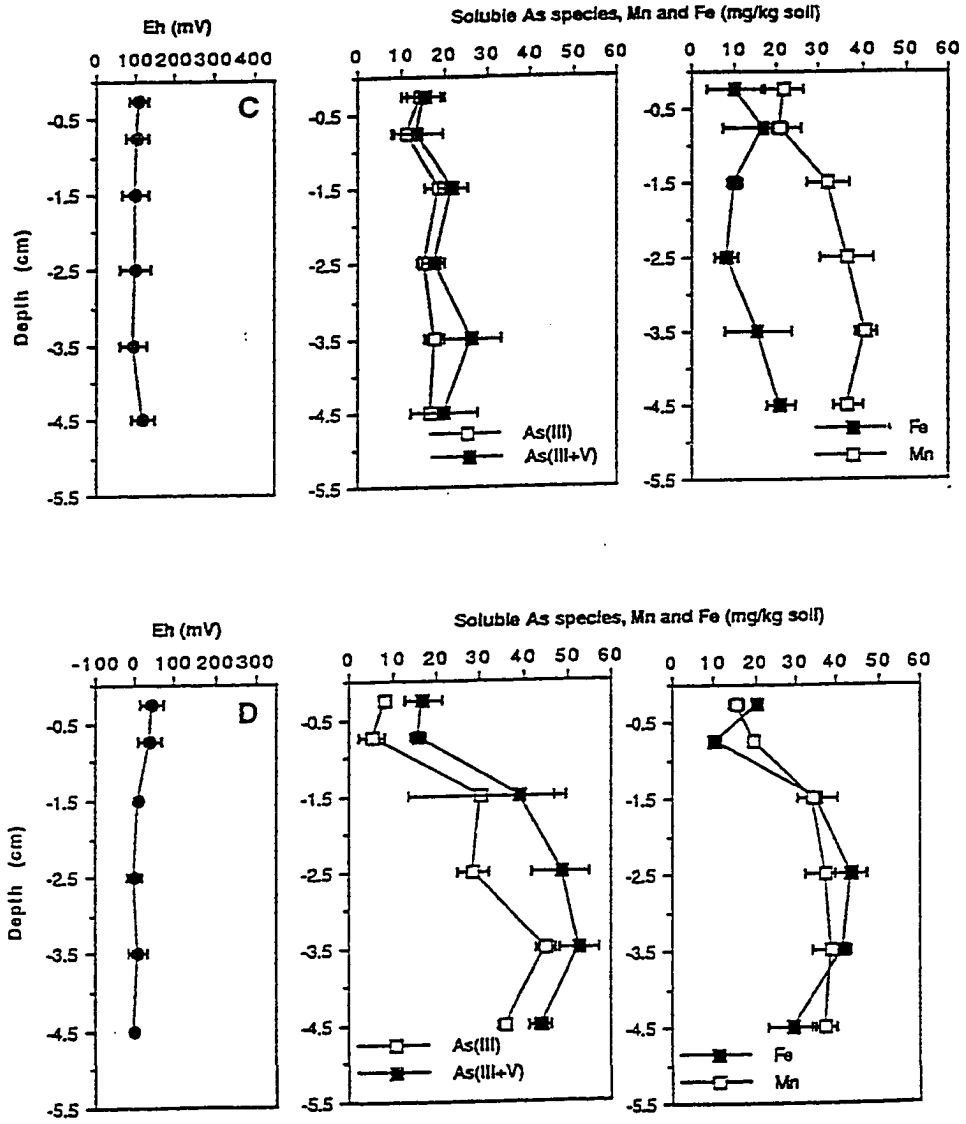

Figure 2: Vertical distribution of Eh, soluble As species, Mn, and Fe. C) after 15 days of flooding (pH = 7.0 ± 0.2). D) after 35 days of flooding (pH = 7.0 ± 0.3). Note changes in scale.

further increase in As concentrations. Up to 10% of the total As present in the soil became soluble.

Although thermodynamically unfavorable, a considerable amount of As(V) was observed under reduced conditions after solubilization of the ferric hydroxide layer (Figure 2C, D). A similar disequilibrium speciation of As observed in reducing waters of a stratified lake (Seyler and Martin, 1989) was attributed to the slow kinetics of the arsenate-arsenite transformation. No detailed information is currently available on the kinetics of As(V) reduction in soils. Although microbial and chemical processes are taking place simultaneously in soil, our study indicates that As(V) served as an effective electron acceptor in microbial mineralization of organic matter, and thereby became reduced to the more mobile and toxic As(III) species. There is some indication that the reduction occurs quickly at lower As concentrations (Figure 2B) but becomes considerably slower at elevated As concentrations (Figure 2C, D). A possible explanation for the slower and incomplete As(V) reduction at lower Eh levels is the competition of Fe(III) as a terminal electron acceptor in microbial respiration.

Another possible explanation for the high As(V) concentrations under reduced conditions is the abiotic oxidation of As(III) by MnO_2. Mn(IV)oxide has been shown to be a very effective oxidant with respect to As(III) in both natural waters and sediments (Oscarson et al., 1980, 1981). Assuming no other reactions take place, every mole of Mn(IV) in the solid phase being reduced to Mn(II) results in the oxidation of one mole As(III) to As(V). Vertical distributions of As and Mn in Figure 2B indicate that the process described above is not of major importance in our soil. Although Mn was reduced, As(III) remained the predominant

soluble As species. This was confirmed during the experiments involving equilibration of the soil under controlled Eh conditions, as illustrated below (Table 1).

Possible arsenic mineral saturation was evaluated by calculating ion activity products (IAP) of various metalarsenates through the use of the equilibrium computer model (PC version 1.23) GEOCHEM (Sposito and Mattigod, 1979). Analytical concentrations of the major cations, metals, and P were put in as total concentrations, as measured on the ICP. Carbonate content was estimated from titration alkalinity determinations and As(V) was obtained from the hydride generation technique. During computations, ionic strength corrections were made using the extended Debye-Huckel expression and, activity of the species were generated. No solids were allowed to precipitate. On a second run, solid phases were allowed to precipitate or dissolve as a double check on possible phases which were not considered in the IAP calculations. Since chemical analysis did not differentiate between Fe(III)/Fe(II) and Mn(IV)/Mn(II), the appropriate redox reactions were included. Calculated IAP of $(Al^{3+})(AsO_4^{3-})$, $(Ca^{2+})_3(AsO_4^{3-})_2$, $(Mg^{2+})_3(AsO_4^{3-})_2$, $(Mn^{2+})_3(AsO_4^{3-})_2$, and $(Fe^{3+})(AsO_4^{3-})$ were compared with their most recent tabulated solubilty products (Dove and Rimstidt, 1985; Sadiq et al., 1983). Other metalarsenates (Cu, Ni, Pb) were ignored because the soluble concentrations of the corresponding metals were very low (< 0.2 mg kg^{-1} soil). Under oxidized conditions, soil extracts were undersaturated (several orders of magnitude) with respect to Al, Ca, Mg, Mn, and Fe arsenate minerals. The activities of Al, Mn and Fe were limited by the formation of their hydroxides. Although the experimental data clearly indicated that As solubility was mainly controlled by an iron phase, the

Fe(III) concentration in solution was not sufficient for precipitation of $FeAsO_4$. Furthermore it has been predicted (Dove and Rimstidt, 1985; Sadiq et al., 1983) that an $FeAsO_4$ mineral formed in soil incongruently will dissolve to iron hydroxide and soluble arsenate, according to the following eq.:

(1) $FeAsO_4.2H_2O + H_2O = H_2AsO_4^- + Fe(OH)_3 + H^+$

Interpretations of the experiment, and equilibrium thermodynamic calculations indicate that As solubility was controlled through several different mechanisms. At higher redox levels (>100 mV) As solublity was controlled by adsorption-desorption reactions as influenced by changes in its redox state (Figure 2B). Desorption of As was occurring simultaneously with the reduction of As(V) to As(III). It is known that Al, Fe and Mn oxides all sorb As(V), and to a lesser extent As(III), with Al and Fe oxides sorbing more than Mn oxides (Pierce and Moore, 1982; Oscarson et al., 1981). Although our results do not indicate which solid surfaces control the As adsorption phenomena in the soil, it is likely that the above mentioned oxides are directly involved. Under moderately reduced conditions (0-100 mV) As solubility was controlled by the dissolution of iron oxyhydroxides (Figure 2C, D). It appears that As(V) was released upon solublization of the hydroxides and slowly reduced to As(III). Although it is very difficult to distinguish between adsorption and coprecipitation reactions without direct examination of the solid surfaces involved (Evans, 1989; Sposito, 1986), consideration of the molar Fe/As ratio's released upon reduction suggests that As was coprecipitated with the Fe oxyhydroxides. The dissolution of Fe oxyhydroxides was earlier proposed to control As mobility in lake waters (Seyler and Martin, 1989) and sediments (Aggett and O'Brien, 1985;

Aggett and Roberts, 1986). The net effect of adsorption and/or coprecipitation is to increase the redox stability of As since lower Eh values become necessary for the As(V)-As(III) transformation to occur. The release of high concentrations of Mn upon reduction and the slow kinetics of arsenate-arsenite transformations made the precipitation of a $Mn_3(AsO_4)_2$ phase under reduced conditions a likely event, as was indicated by GEOCHEM. The following reactions, based on thermodynamic data (Lindsay, 1979; Sadiq et al., 1983), illustrate this:

		log K
(2)	$3x\ [MnOOH + 3H^+ + e^- = Mn^{2+} + 2H_2O]$	3x 25.27
(3)	$3Mn^{2+} + 2HAsO_4^{2-} = Mn_3(AsO_4)_2 + 2H^+$	8.51
	---	
(4)	$3MnOOH + 2HAsO_4^{2-} + 7H^+ + 3e^- = Mn_3(AsO_4)_2 + 6H_2O$	84.32

After rearranging eq.(4), assuming activities of solid phases and H_2O equal to 1, and substituting values of 7 and 0.5 for respectively pH and pe (Eh=30 mV) we obtain log $a_{(HAsO4^{2-})}$ = -16.91. From this expression it can be seen that, upon reduction, MnOOH becomes unstable and very small amounts of soluble As(V) are sufficient to obtain supersaturation with respect to a Mn arsenate phase. The formation of $Mn_3(AsO_4)_2$ could set an upper limit for dissolved arsenate concentrations under reducing conditions. Although thermodynamically favorable, the formation of such a compound could be inhibited due to slow kinetics. Since H^+ are consumed in eq.(4) the pH will tend to increase.

The soil was never sufficiently reduced to cause the further reduction of As(III) to elemental As or AsH_3 (Fig 1). Sulfide

concentration stayed well below the detection limit (0.05 ppm) of our analytical technique and its influence on As solubity in the soil could therefore be neglected.

Redox-pH chemistry of Arsenic

The redox-pH chemistry of As was studied by equilibrating soil suspensions under controlled Eh-pH conditions. Figure 3 shows the species distribution of As at three suspension pH levels (5.0, natural, and 8.0) in combination with four different redox levels (-200, 0, 200, and 500 mV). After about 10 days of incubation, the preselected redox and pH were reached and maintained during a 2-week period. Upon acidification of the soil to pH 5, strongly reduced conditions (-200 mV) couldn't be achieved, and were therefore not included.

Both redox status and pH affected the speciation and solubility of As. At redox potentials of 200 and 500 mV, As(V) was the major dissolved As species constituting > 95% of the total soluble As. Upon reduction (0 and -200 mV), As(III) became the major dissolved As species, although considerable concentrations of As(V) remained, and As solubilty generally increased. Up to 40 % of the total As present in the soil became soluble. While the first experiment gave an idea of As transformations under natural conditions, the stirred suspension experiment indicated maximum transformations rates. Similar mechanisms controlling As solubility were observed in both experiments. Table 1 contains data obtained during two of the controlled Eh experiments. The increase in arsenic solublity before the reduction of the iron oxyhydroxides was characterized by a reversal in As speciation. Although Mn was reduced after 3 days of incubation, As(III) remained the dominant

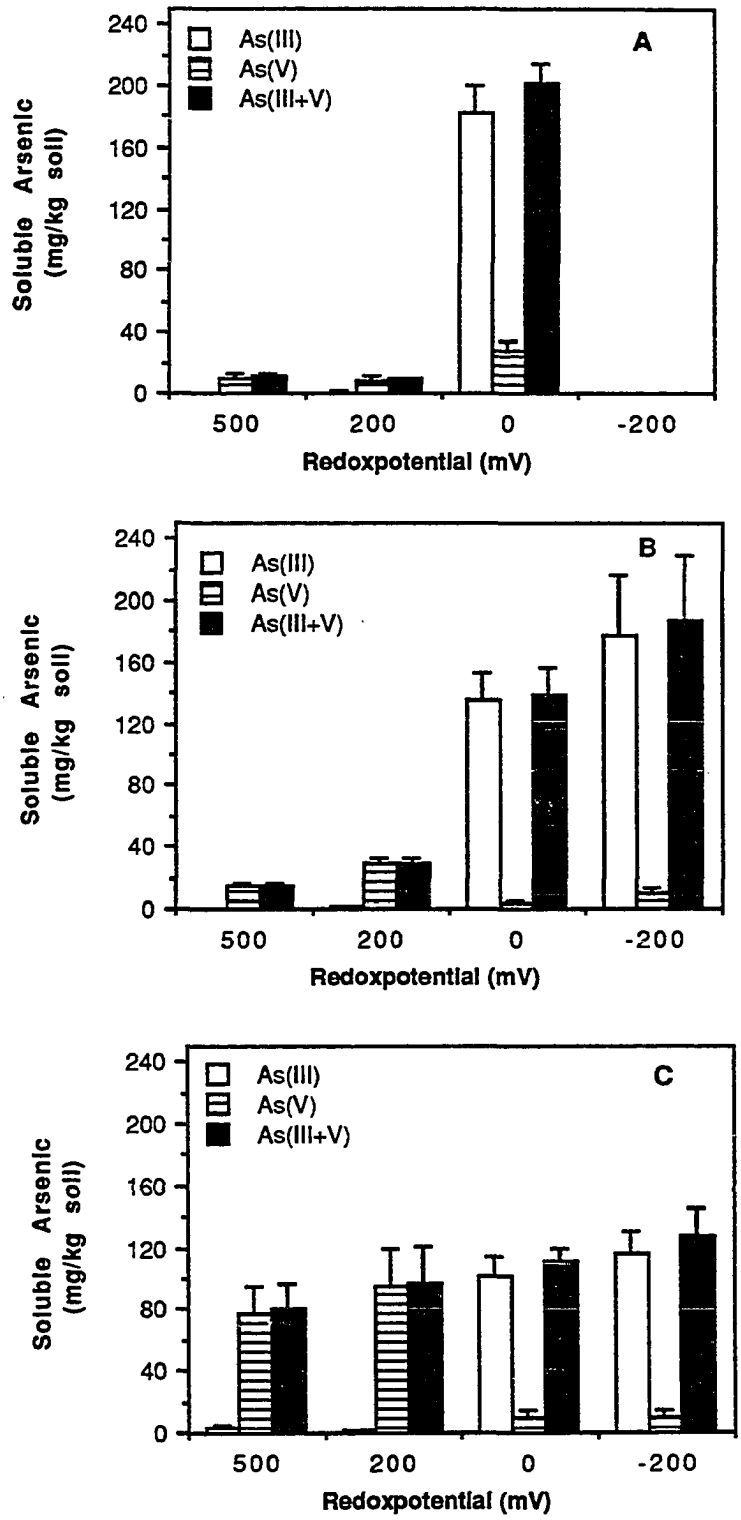

Figure 3: Distribution of soluble arsenic species after a 24-day equilibration period under controlled redox and pH conditions. A) at pH 5.0. B) at natural pH (5.2 for 500 mV, 6.7 for 200 mV, 7.0 for 0 mV, and 7.2 for -200 mV). C) at pH 8.0.

Table 1. Concentration of soluble As species, Mn, and Fe as function of soil redox-pH conditions.

Day	pH	Eh	As(III)	As(V)	Mn	Fe
			mg kg^{-1} soil			
0	5.6	340 mV	1.40	5.60	1.90	17.5
3	6.7	100 mV	46.8	3.10	20.8	15.3
6	6.8	20 mV	76.5	6.60	21.2	72.0
0	5.8	440 mV	0.90	7.90	2.40	27.3
3	6.6	80 mV	34.3	1.20	17.4	29.5
6	7.0	-100 mV	69.4	3.40	16.2	75.8

As species suggesting that the abiotic oxidation of As(III) to As(V) by Mn(IV) compounds was not important in our soil. A sharp increase of soluble As concentrations coincided with the reduction of Fe oxyhydroxides and As(V) was slowly reduced.

Interesting information was obtained from the alkaline (pH 8) equilibrations. Under oxidized conditions soluble As concentrations were as much as 3 times higher than in the incubations at lower pH. Almost all As was present as As(V). This can be explained by the pH dependent adsorption characteristics of As(V) onto the oxide surfaces (Evans, 1989; Pierce and Moore, 1982). The increasing negative surface charge of the oxides with increasing pH facilitated the desorption of arsenate. Under reducing conditions As(III) became the major dissolved species with total soluble As being less in the more acidic equilibrations. The reason for this is somewhat unclear. An incomplete or slower reduction of Fe oxyhydroxides under alkaline conditions (Figure 1) could be responsible for the lower As concentrations observed. At pH 8, dissolved Fe concentrations did not significantly increase upon reduction. Futhermore, the presence of soluble organics under alkaline conditions (pH 8.0) and the formation of iron oxyhydroxides-organic matter complexes could have retarded Fe reduction (Theis and Singer, 1974), and the release of As into solution.

In summary, redox potential and pH were shown to control the speciation and solubility of arsenic in a contaminated soil. Both parameters are, therefore, important in assessing the fate of As-containing compounds in soil. At higher redox levels, As(V) was the predominant As species and As solubilty was controlled by an adsorption mechanism. Alkaline conditions and/or reduction of As(V) to As(III) can

lead to a desorption of As. Under moderately reduced conditions, (0-100 mV) As solubility was controlled by the dissolution of iron oxyhydroxides. Data indicate that As was coprecipitated [as As(V)] with the oxyhydroxides and released upon their reduction. Due to the slow kinetics of the As(V)-As(III) transformation, a considerable amount of the thermodynamically unstable As(V) species was observed under reducing conditions. This slow transformation rate and the release of high concentrations of Mn upon reduction make the precipitation of a Mn_3AsO_4 phase possible. In planning disposal of As-containing wastes, consideration should be given to maintaining high redox and non-alkaline conditions necessary for minimum As solubility.

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SUMMARY AND CONCLUSIONS

Over the years it has become evident that in assessing the toxicity, and the behavior of trace elements, such as selenium (Se) and arsenic (As), in the environment it is important to know which chemical form of the element is present. Presently, little quantitative data are available on the distribution, and stability of As, and especially Se species in soils and sediments. Both the lack of experimental data and the importance of a better understanding of Se and As chemistry in wetland soils and sediments warranted a study dealing with the speciation, species transformations, and solubility of Se and As.

First, a sensitive analytical technique was developed that allowed for the accurate determination of Se and As species commonly encoutered in natural waters, soils, and sediments. Secondly, the speciation and redox chemistry of Se and As was studied in selected soils and sediments.

Selenium and As species were determined using a hydride generation/ trapping / separation technique followed by atomic absorption spectrophotometry detection. The detection limits were 5 ng for Se and 2 ng for As, respectively.

Analytical procedures were described for the determination of dissolved dimethyl selenide (DMSe), selenite [Se(IV)], oxidized methylated organo Se-compounds (Ox.MSe), selenate [Se(VI)], and elemental selenium and selenide [Se(0,-II)]. Briefly, the volatile methyl species were removed from the sample with an inert stripping gas. The inorganic froms were selectively reduced to H_2Se, and also stripped from the sample. A liquid N_2 trap was used to collect both volatile

methylated species and generated H_2Se. Separation of methylated species and H_2Se was accomplished by controlled heating of the sample trap. After selective volatilization from the trap, the Se species were detected in a flame-in-tube atomizer aligned in the optical beam path of the atomic absorption spectrophotmeter (AAS).

A similar procedure was used to detect and quantify As species [arsenite, As(III); arsenate, As(V); monomethylarsonic acid, (MMAA); and dimethylarsinic acid, (DMAA)]. After a pH-selective reduction, the As species were condensed in a U-tube filled with a gas chromatographic packing immersed in liquid N_2. The species were then separated by slow warming of the sample trap and measured with an AAS. The use of the gas chromatographic support led to an efficient and reproducible arsine separation.

The influence of redox potential and pH on Se speciation, and solubility was studied in Se contaminated sediments from Kesterson Reservoir (CA) and Hyco Reservoir (NC). Sediment suspensions were equilibrated under controlled redox and pH conditions, and the Se concentration and species distribution were determined. In order to better validate redox measurements and to obtain as much information as possible about Se chemistry in these sediments, the suspensions were also analyzed for major cations, metals, and anions.

Dissolved Se concentrations in reduced (-200 mV) Kesterson Reservoir sediment suspensions were low and Se(-II,0) comprised 80 - 100% of the total soluble Se. Upon oxidation of the sediment suspensions, however, Se concentrations increased substantially. Oxidation of Se(-II,0) to Se(IV) occurred at a redox of approx. 0 mV, and led to an increase in dissolved Se concentrations. Under moderately

reduced conditions Se(IV) was the dominant Se species present. At redox levels above 200 mV, Se(IV) was further oxidized to Se(VI). Although thermodynamically unstable, a considerable amount of Se(IV) remained present under highly oxidized (450 mV) conditions. Under the highly aerobic conditions, Se solubility reached a maximum. Selenium solubility increased approx. 20 times upon oxidation of the sediment from -200 to 450 mV.

Results obtained during the experiments with the Hyco Reservoir sediments confirmed the importance of sediment redox potential in the study of Se biogeochemistry. In the Hyco Reservoir sediments, Se solubility was greatest under highly oxidized (500 mV) conditions and decreased significantly upon reduction of the sediment suspensions. As in the Kesterson Reservoir study, changes in the Se species distribution led to Se solubility changes. Selenate [Se(VI)] was the predominant dissolved Se species at 500 mV. At 200 and 0 mV, Se(IV) became the most stable oxidation state of Se. Under strongly reduced conditions (-200 mV) oxidized Se species were no longer present, and soluble Se decreased to a nearly detectable level. The concentrations of water soluble Se species were also found to be pH dependent. In both sediments, an increase in pH led to increased dissolved Se concentrations. In general, the species distribution of Se as affected by sediment redox potential and pH was consistent in both studies.

The data obtained during the experiments with the Kesterson Reservoir sediments suggest that the oxidation and chemical weathering of iron sulfides led to an increase in dissolved Se concentrations. The disappearance of oxidized Se species upon reduction of the Hyco Reservoir sediments indicated that Se solubility under reduced

conditions could be controlled by the formation of elemental Se and / or metal selenides. Based on this information, selected thermodynamic data were used to predict Se behavior in anoxic sediments and soils. Redox-pH diagrams displaying mineral stability boundaries in the Fe-S-Se-H_2O system at 25° C and 1 bar total pressure were constructed. Under reducing conditions, elemental Se and the formation of FeSe or $FeSe_2$ could control Se solubility. Native Se was found to have a wide stability field, particulary under acid conditions. Under weakly acid to alkaline conditions, however, the formation of iron selenides is thermodynamically favored. If we assume that selenide can substitute for sulfide in a solid solution phase, precipitated FeS will contain a FeSe component. Under conditions of FeS_2 formation, both FeSe and $FeSe_2$ are thermodynamically unstable, and elemental Se is produced.

The experimental data also clearly illustrates the importance of biomethylation in Se chemistry. Dissolved DMSe and oxidized methylated Se compounds were detected under aerobic and moderately reduced (500 - 0 mV) conditions. In the Kesterson Reservoir sediments, DMSe comprised 15 % of the total soluble Se, while dissolved oxidized methylated Se compounds made up 5 % of the total soluble Se concentration. In the oxidized Hyco Reservoir sediments, DMSe constituted up to 36 % of the dissolved Se. Oxidized methylated Se compounds were present in only minor amounts.

The speciation and redox chemistry of As was studied in Hyco Reservoir (NC) sediment suspensions and in an As contaminated soil from Kolin (La). Redox potential and pH exhibited a major impact on As speciation and solubility in both studies. In contrast to selenium, arsenic solubility reached a maximum under reduced conditions. An

alkaline pH resulted in greater dissolved As concentrations. Although the developed analytical technique was optimized for the determination of MMAA and DMAA, no organic arsenicals were detected.

In oxidized Hyco Reservoir sediments, arsenic solubility was low and 87 % of the As in solution was present as As(V). Upon reduction, As(III) became the major dissolved As species, and As solubility increased. Total As in solution increased approx. 25 times upon reduction of the sediment suspensions from 500 to -200 mV.

Valuable information on the biogeochemical processes controlling As solubility was obtained from experiments conducted with the Kolin soil. Interpretations of the experiment, and equilibrium thermodynamic calculations indicate that As solubility was controlled through several different mechanisms. At redox levels greater than +100 mV, As solubility was controlled by adsorption-desorption reactions as influenced by changes in its oxidation state. Desorption of As occurred simultaneously with the reduction of As(V) to As(III). The dissolution of iron oxyhydroxides controlled As solubility at redox levels between +100 and 0 mV. Arsenic (V) released upon solubilization of the hydroxides, slowly reduced to As(III). The observed slow kinetics of the As(V) - As(III) transformation and the high concentrations of Mn present indicate that, under reduced conditions, As solubility could be controlled by a $Mn_3(AsO_4)_2$ phase. Upon reduction to -200 mV, the As content increased 13-fold as compared to 500 mV.

Both pH and redox potential were found to affect speciation and solubility of Se and As in soil or sediment-water systems. Therefore, changes in redox-pH conditions can significantly influence Se and As bioavailability and toxicity. This is of great importance in wetland

soils and sediments. Water table fluctuations in wetlands, excessive soil drainage, and upland disposal of dredged sediments all lead to changing redox-pH conditions, which in turn will affect the chemistry and bioavailability of environmental important trace elements, such as Se and As. Results generated in this study identified redox-pH conditions which can limit or enhance Se and As translocation and movement in the environment.

APPENDIX

LETTERS OF PERMISSION TO REPRINT

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17 October 1990

Dr. Patrick H. Masscheleyn
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Baton Rouge, LA 70803-7511

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Volume 20, 1991, (page numbers unknown). Patrick H. Masscheleyn, Ronald D. Delaune, and William H. Patrick, Jr.

Article, "Arsenic Speciation Using a pH Selective Hydride Generation/Separation Technique Followed by Atomic Absorption Spectrophotometry Detection."

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October 24, 1990

Mr. Patrick H. Masscheleyn
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Dear Mr. Masscheleyn:

Thank you for your letter of October 10, in which you requested permission to include in your thesis, your paper, "Transformations of Selenium as Affected by Sediment Oxidation-Reduction Potential and pH," from *Environmental Science & Technology* 1990, *24*, 91-96.

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VITA

Patrick H. Masscheleyn was born on October, 18, 1962, in Veurne, Belgium. In 1985 he graduated form the State University of Ghent, Belgium as an Engineer in Agricultural Chemistry. He then entered the interdepartmental program in Environmental Studies at the State University of Ghent, Belgium. In 1987 he received the degree of Engineer in Environmental Sanitation. Following graduation, he was employed by the Laboratory for Analytical and Agrochemistry, State University of Ghent, Belgium. In August 1987, he obtained a Fulbright Scholar Award and came to the Louisiana State University, Baton Rouge, for graduate studies. While at Louisiana State University, he received the Joe Lipsey Sr. memorial scholarship and the Lyle St. Amant Award. He is presently a candidate for the degree of Doctor of Philosophy.

DOCTORAL EXAMINATION AND DISSERTATION REPORT

Candidate: Patrick H. Masscheleyn

Major Field: Marine Sciences

Title of Dissertation: Speciation and redox chemistry of selenium and arsenic in wetland soils and sediments.

Approved:

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

Date of Examination:

November 2, 1990